

PYROLYSIS GAS CHROMATOGRAPHY OF SOME POLYMERIC MATERIALS

Lena Tröjer



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Lena Trojer, fil.kand., B1

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Abstract The influence of the <u>chamber temperature</u>, the carrier gas flow and the pyrolysis <u>temperature-time profile</u> on the pyrolysis result was investigated for <u>polystyrene</u> as a test substance and employing a <u>foil pulse pyrolyzer</u>. The carbonization of polystyrene during pyrolysis with a platinum foil pyrolyzer was estimated by the amount of <u>hydrogen</u> formed. Conditions to obtain good precision in pyrolysis of insoluble samples was investigated for <u>vulcanized styrene-butadiene rubber</u>. Quantitative analysis of the composition of the copolymer in the vulcanizate could be performed using <u>unvulcanized reference copolymers</u>. Different <u>sulfur bridges</u> in vulcanized isoprene rubber was studied by the <u>sulfur-containing pyrolysis products</u> detected with a sulfur selective flame photometric detector. The pyrolysis gas chromatography technique was also applied to stationary phases for reversed-phase high-performance liquid chromatography. The stationary phases, i.e. different hydrocarbons, bonded to silica gel was characterized for the chain length of the hydrocarbon, the functionality of the silanizing agent, <u>post-silanization</u> and <u>polymerization</u>.			
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Lena Trojer, Dept of Analytical Chemistry,
University of Lund, P.O.Box 740, S-220 07 Lund, Sweden

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Till Magnus och Martin



This thesis summarizes the work presented in the following papers, referred to in the discussion by the Roman numerals I-VI.

- I The Influence of the Gas Chromatographic and Pyrolysis Conditions on the Obtained Pyrolysis Results. Exemplified by Polystyrene.
I. Ericsson and L. Trojer
Submitted to J. Anal. Appl. Pyrol.
- II Hydrogen Formation during Pyrolysis of Polystyrene.
L. Trojer
J. Anal. Appl. Pyrol., 2(1981)353
- III Pyrolysis Gas Chromatography Studies of Insoluble Samples. Exemplified by Vulcanized Styrene Butadiene Rubber.
L. Trojer and I. Ericsson
J. Chrom. Sci., 16(1978)345
- IV A Study of Sulfur Bridges in Filled Natural Rubber Vulcanizates by Pyrolysis Gas Chromatography with Flame Photometric Detection.
E. Andersson, I. Ericsson and L. Trojer
Submitted to J. Appl. Polym. Sci.
- V Characterization of Reversed Phase HPLC Stationary Phases by means of Pyrolysis Gas Chromatography.
L. Hansson and L. Trojer
J. Chromatogr., 207(1981)1
- VI A Study of Polymerization and Post Silanization of Octadecylsilyl Phases Bonded to Silica Gel.
L. Trojer and L. Hansson
In manuscript.

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INTRODUCTION

Pyrolysis, i.e. the thermal degradation of a sample in an inert atmosphere into one or several products, has been shown to be a useful tool for investigation of a wide range of different, preferably non-volatile, materials.

The equipment for pyrolysis varies considerably in performance and function. Three types of apparatus are most frequently used and they are based upon i) induction heated filaments ii) resistively heated filaments or foils and iii) furnace heating [1]. The two first modes are classified as pulse-mode and the last as continuous-mode [2] pyrolyzers. The pyrolysis units are mainly used in conjunction with a mass spectrometer (PyMS), an infrared spectrometer (PyIR), a gas chromatograph (PyGC) or a gas chromatograph connected to a mass spectrometer (PyGCMS). The technique of PyGC has found widespread use because of its simplicity and usefulness for quantitative studies, which otherwise are difficult to perform, e.g. with PyMS.

Two pulse-mode, resistively heated pyrolyzers coupled to a gas chromatograph were used in the present studies.

The use of pyrolysis as an analytical technique is, however, limited by the lack of a broad standardization praxis. Inter-laboratory correlation trials have been performed [3]. What is learned from these tests, is the importance of the experimental conditions and their influence on the product yields.

Further investigations of the effects of these conditions can provide the basis for improving the method and thus expand the range for pyrolysis as an analytical technique.

In this context, important parameters to be considered are the actual temperature-time profile, the material of the sample holder and the temperature of the surroundings. These are parameters connected to the construction and function of the pyrolysis equipment.

An important feature of the temperature-time profile is the temperature rise time [4]. It is critical especially for high temperatures, because pyrolysis is then normally carried out during the heating of the sample. For comparative studies, the exact pyrolysis temperature has to be known. Large discrepancies between nominal and actual temperatures have been reported [5,6].

The material of the sample holder is important with consideration to possible catalytic effects. The effect of the material has been studied for Pt, Fe and Ni [7]. Pt showed larger catalytic effects than Ni and Fe. A relatively high degree of carbonization, i.e. degradation into carbon and hydrogen, was also obtained for Pt.

Other important parameters are those concerning the sample. The influence of the sample size on the quantitative results has been studied for sample weights between nanogram and milligram [8]. The detection limit was decreased by adding a known amount of another polymer, which reduced the catalytic effect of the metal filament.

The temperature-time profile of the sample has been estimated [9] and, for samples thinner than 1 μm , is almost the same as of the pyrolyzer.

A well defined PyGC system admits kinetic measurements [9,10]. As a relative measure the degradation rate constants can conveniently be utilized for qualitative and quantitative studies [11].

In spite of the lack of exact knowledge about the above mentioned parameters, pyrolysis has been applied to a great number of extremely varying analytical problems. It has been used to investigate inorganic and organic material, synthetic polymers, biopolymers and organic geopolymers [1].

The papers in this thesis deal with the influence of different experimental conditions on the pyrolysis results and with application of the PyGC technique to compounds difficult to analyse namely vulcanized rubber and chemically bonded stationary phases.

EQUIPMENT

In paper I, III and IV a foil pulse pyrolyzer was utilized. The pyrolyzer was developed by Inger Ericsson and has been described in detail elsewhere [12]. It consists of a Pt foil (0.0125 x 2.6 x 15 mm), which can easily be changed and calibrated. The foil is heated

by two current pulses. The first, usually 8 ms, brings the foil to the desired temperature and the second, the length of which can be varied, keeps the temperature at a constant and choosen level.

The temperature of the foil was determined by registration of the resistance change of the foil and by a calibrated photodiode [13].

In paper II, V and VI a CDS 150 pyroprobe was used. The work presented in paper II was performed utilizing a probe with a 0.0125 x 1.6 x 38 mm Pt foil and in paper V and VI a probe with a Pt coil, within which a quartz-tube with a sample holder was placed. The foil and coil were heated by a current pulse. The magnitude of the pulse was determined by the resistances in a Wheatstone bridge, in which the foil or the coil constitutes one branch.

The two different pyrolyzers were mounted on the injection port of either a Varian 1860 or a 3700 gas chromatograph. Peak areas were normally measured by a Varian CDS 101 electronic integrator. In some cases peak areas were measured by an OTT-planimeter.

For identification of pyrolysis products the pyroprobe was mounted on the GC part of a Finnigan 4021 mass spectrometer.

3. VARIATION IN THE PyGC CONDITIONS

The influence of different conditions on the pyrolysis results were studied for polystyrene as a test substance. Polystyrene is well recognized in the field of pyrolysis. A survey of published data is given in paper I. In addition to the main purpose of this work the results can contribute to an increased understanding of the thermal degradation of polystyrene.

3.1 GC conditions

The products obtained from pyrolysis of polystyrene can be found in a molecular weight range from 2 (H_2) to above 312 (styrene trimer) and in different isomeric forms. To be able to separate most of these products a good column and temperature programming has to be used. A short, 1.5 m, column with only 2% Apiezon L on an inert support was sufficient (Fig. 2, paper I). Ultrabond 20 M was superior to a silanized silica as inert support. For separation of low molecular weight products a Chromosorb 102 column run isothermally at a low temperature was adequate (paper II).

The gas flow rate affects principally the high molecular weight products (Fig. 2, paper I) provided that the pyrolysis temperature is adjusted. A higher gas flow rate decreases the possibilities for condensation and an increased yield of the high molecular weight products are thus obtained.

3.2 Temperature of the pyrolysis chamber

Especially when studying pyrolysis products of high molecular weight, the temperature of the pyrolysis chamber is important [14]. The increasing yield of predominantly styrene dimer and trimer with chamber temperatures from 115 to 175°C are illustrated in Fig. 2, paper I. The influence of the chamber temperature has also been considered in paper II, where the pyroprobe was employed.

In additional studies to papers I and II, polystyrene was pyrolyzed with three different pyrolyzers. The two units previously described and a third one, a Curie-point pyrolyzer (Philips), were used. The temperature of the chamber of the foil pulse pyrolyzer and the pyroprobe were set to 115°C. The chamber temperature of the Curie-point pyrolyzer could not be controlled and was lower than 115°C. At pyrolysis temperatures around e.g. 770°C and pyrolysis times of 5 seconds a significant yield (ca 8%) of styrene trimer was obtained using the Curie-point pyrolyzer. A very small yield of the trimer was obtained, when the pyroprobe was used at the same nominal conditions. No trimer was found, when the foil pulse pyrolyzer was employed. In spite of the lower chamber temperature in the Curie-point pyrolyzer, where severe condensation is expected, high boiling-point products were indeed obtained. This was probably due to the higher carrier gas velocity, which implies that the large fragments were transported further onto the column to a much larger extent than for the other pyrolyzers. The volume and cross-section of the chamber is smaller for the Curie-point pyrolyzer. Condensation did also occur in the Curie point pyrolyzer, where after pyrolysis a thin film formed on the inner walls of the chamber (glass tube) could be observed.

For some analytical problems a high chamber temperature may be unfavourable. This was the case in the study of vulcanized rubber. Degradation of the sample before the desired pyrolysis could be observed (paper IV), when a high temperature was used. The temperature ought to be lower than the vulcanizing temperature, especially if the influence of the vulcanizing process is to be studied.

3.3 Variation in temperature-time-profile

The foil pulse pyrolyzer constitutes a well defined and easily varied system. It is therefore possible to study the influence of different temperature-time profiles.

In paper I, temperature-time profiles for four different modes were investigated. They were obtained by

- i) variation of the pyrolysis end temperature.
- ii) changing the pyrolysis time maintaining a constant rate of variation of the temperature.
- iii) changing the rate of variation of temperature maintaining a fixed final temperature.
- iv) variation of the total heating time.

When the pyrolysis end temperature was varied, the yields of the main product - styrene - attained a maximum at 800°C. The yields of the dimer (Fig. 5, peak 11) and of the trimer did not show any maxima. They decreased with increasing temperature. The total yield indicates condensation of very large fragments before the optimum temperature was attained and an increasing degree of carbonization afterward.

It ought to be stressed that a lot of information is gained if absolute values or values relative to the detector calibration are used. A pyrolysis system with good precision is, of course, required.

An example of the advantage of using absolute values is given in paper I, where the total or monomer yields for polystyrene with different molecular weight were compared. The total yield for samples with MW 2100 was about 50% of the total yield for samples with MW 20 800 or higher at e.g. 700°C (Fig.4B). This could not have been seen, if only relative values were available (Fig.4A). The reason for this special behaviour in the thermal degradation of very low molecular weight polystyrene seems to be formation of relatively large fragments during pyrolysis in a great extent. These fragments were condensed and escaped detection. Thermogravimetric analysis confirmed this conclusion.

Formation or further degradation of pyrolysis products was studied with the second mode of the temperature-time profile. The pyrolysis final temperature was fixed at 1440°C, which was attained in 8 ms, and pyrolysis were performed at different times from 4.5 to 8 ms. Styrene, as the main pyrolysis product, was degraded after about 5.3 ms ($\sim 940^{\circ}\text{C}$). High molecular weight polystyrene gave larger styrene yields in this mode than those obtained in the first mode. A comparison of the total yields given by the two modes shows that at shorter temperature rise times, less carbonization was observed. On the opposite, for low

molecular weight polystyrene both total and styrene yields were smaller with the second mode. This is a consequence of the specific thermal degradation of the low molecular weight polystyrene. The larger fragments formed suffered less secondary degradation at shorter rise times. Longer rise times implied further degradation of these fragments, giving products small enough not to condense and thus able to be detected. The total yield was therefore increased.

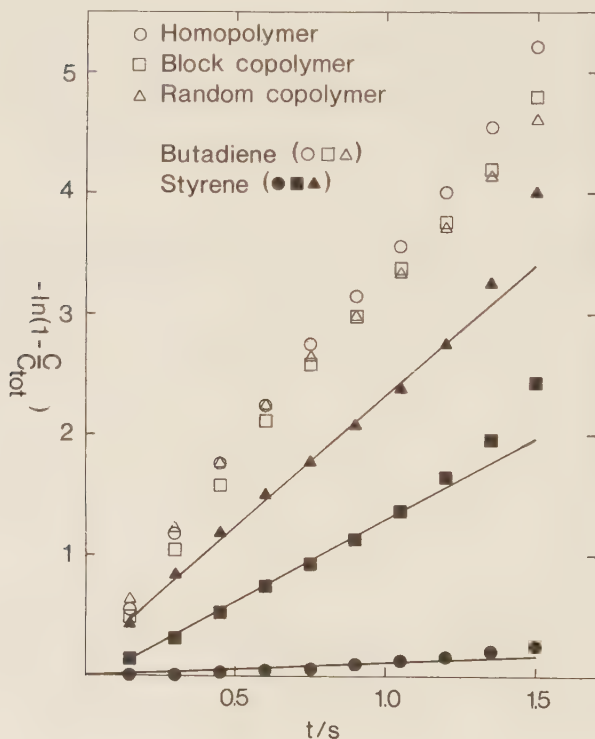
Continuous product formation during the heating to 1440°C could be observed for peak no 1 (Fig. 5, paper I). It was a mixture of C_1 to C_5 hydrocarbons. Toluene and peak no 14, probably a rearranged styrene dimer, were also continuously formed up to ca 1300°C .

In the third mode, the final temperature was fixed at 750°C and the rise times varied between 8 ms and 1 s. No large effects were observed. At shorter times the degradation was performed at higher temperatures and with less secondary effects. On the opposite, degradation at a lower temperature but with more secondary decomposition resulted for longer rise times.

The influence of the pyrolysis time, the fourth mode of the temperature-time profile, was quite drastic at high temperatures. At 1210°C the total yield, for high molecular weight polystyrene, decreased with about 30% between 8 ms and 5 s. At 750°C the influence of the pyrolysis time was minor.

3.4 Kinetic studies

Another advantage of a high precision pyrolysis system is the potential to make kinetic measurements. The degradation rate constant can for instance be used for determination of the structure of copolymers. An example is presented in the figure.



Homo- and copolymers (25/75 w/w) of styrene-butadiene rubber were subjected to sequential pyrolysis [10] at 545°C with a pulse time of 150 ms. The decomposition of polystyrene and polybutadiene is a first order reaction [13] (at the temperatures used). At constant temperature the rate equation

$$(1) \quad -\ln\left(1 - \frac{C}{C_{\text{tot}}}\right) = kt$$

is then valid.

C is the yield of the product studied after the pyrolysis time t . C_{tot} is the total yield of the same product after complete degradation and k is the degradation rate constant. The formation rate of the styrene monomer is highly affected by different distribution of the butadiene and the styrene in the copolymer chain.

For butadiene the temperature was too high to show kinetic effects. Furthermore its relative content in the copolymer was in such an excess that even the random copolymer must consist of large blocks of butadiene and thus be similar to a blockpolymer.

The formation rates of the two monomers are in between those from the homopolymers. For styrene, the rate increased in the sequence homo-, block- and random- copolymer, approaching the rate of the formation of butadiene. The rate constant can thus be used as a qualitative evaluation of the type of copolymer.

3.5 Formation of Hydrogen

It is well known that platinum is a catalyst for hydrogenation and dehydrogenation reactions [15]. At high temperatures dehydrogenation prevails [16]. The study of hydrogen formation during pyrolysis of polystyrene presented in paper II was initiated by previous studies on polybutadiene [10].

Especially at high temperatures the total yield was drastically reduced and carbon could be seen on the Pt-foil. One way to estimate the degree of carbonization is to measure the hydrogen formed. Hydrogen can be detected readily by a thermal conductivity detector. This detector could not be interfaced with the gas chromatograph to which the foil pulse pyrolyzer was mounted, and therefore the study was performed using the pyroprobe. The Pt-foil in the pyroprobe was 2.5 times longer than in the foil pulse pyrolyzer.

The main part of the pyrolysis study in paper II was performed at an interface (i.e. pyrolysis chamber) temperature of 115°C . Hydrogen was detected at pyrolysis temperatures between 510 and 980°C . An increasing yield with increased pyrolysis time, in fact longer than the time needed for complete pyrolysis, suggested secondary degradation. This was also indicated by a corresponding decrease in the total yield of hydrocarbonaceous products formed at temperatures of 770 and 980°C .

At a high interface temperature and at pyrolysis temperatures above ca 750°C almost 100% of the pyrolyzed polystyrene could be accounted for. At pyrolysis temperatures of 610°C and lower, where the yield of larger fragments than styrene trimer seems to be significant, the condensation of the former resulted in a non-quantitative recovery, in spite of the high interface temperature.

The activity of Pt, resulting in a high degree of carbonization, seems to be a disadvantage for Pt as material of the sample holder in a pyrolyzer. Compared to other metals [7] Pt is, however, superior because of its inertness and convenience in handling.

4. PyGC APPLIED TO VULCANIZED RUBBER

Vulcanized rubber is a material difficult to analyse by conventional methods. The polymer is crosslinked by sulfur bridges and it is almost impossible to dissolve. Usually the vulcanized rubber is filled with carbon black, which makes it opaque and thus unsuitable for spectrophotometric analysis. The use of PyGC as a promising analytical tool for vulcanized rubber is shown in paper III and IV.

4.1 Vulcanized styrene butadiene rubber

The foil pulse pyrolyzer was utilized in the investigation presented in paper III and hydrocarboneous products were studied. The precision in the pyrolysis of insoluble samples was improved, compared to previous studies, by optimizing the pyrolysis conditions and decreasing the sample size.

The optimum pyrolysis temperature was found to lie between 900 and 950°C, where a small variation in temperature did not affect the yield in any appreciable extent.

Two series of vulcanized styrene butadiene rubber (SBR) were pyrolyzed at 900°C. One series constituted thin, microtome cut samples. For these samples the relative standard deviation was 2.6% for the butadiene peak and 0.80% for the styrene peak. Another series constituted thicker, hand cut samples. The relative standard deviation was then 2.7% for the butadiene peak and 0.92% for the styrene peak.

Vulcanized SBR and pure copolymer SBR showed no qualitative differences in the products detected at the gas chromatographic conditions used. The higher yields for the pure copolymer could be attributed to smaller temperature gradients in the sample. It could also be due to less formation of large fragments, not detected, than for vulcanized SBR.

By using the unvulcanized copolymer as reference samples, quantitative analysis of the composition of the copolymer in the vulcanizate was possible. The relative yield of butadiene was affected by the vulcanization, because sulfur is bonded to the butadiene molecule. For styrene the relative yield nearly coincide for both vulcanized and unvulcanized SBR in a wide temperature range (Fig. 3, paper III). The relative yield of styrene for different unvulcanized SBR was thus used in a calibration graph.

The influence of vulcanization on the hydrocarbaceous pyrolysis products was studied on samples with varying amounts of sulfur and tetramethylthiuram disulfide (TMTD). The yield of butadiene decreased with increasing total amount of sulfur.

4.2 Sulfur bridges in vulcanized isoprene rubber

One important factor in the characterization of vulcanized rubber is the type of sulfur-bridges. There exists few direct methods, which provide chemical information. Physical properties have been measured after exposing vulcanized rubber to chemical treatments, which selectively attack the different types of sulfur-bridges [17]. The sulfur-containing degradation products of the vulcanized isoprene polymer could provide valuable information for the characterization of sulfur-bridges. Improved sensitivity for these products was attained using a flame photometric detector operating in the sulfur mode. The foil pulse pyrolyzer was employed with a modified Pt foil.

Two types of vulcanized isoprene rubber were investigated. In one (A) sulfur/CBS (N-cyclohexyl-2-benzothiazolesulfenamide) and in the second (B) TMTD was used as vulcanizing agent. The former is supposed to give mainly polysulfide and the latter mono- and disulfide links. Reference material was analysed for the cross-links by means of conventional chemical treatments followed by stress strain measurements.

It was found that the two types of vulcanizates exhibited quite different fragmentation patterns i.e. the sulfurous pyrolysis products were the same but their yields were different. The sulfur-containing products were essentially carbon disulfide, thiophene, 2-methyl-thiophene and 3-methyl-thiophene. The thio-phenes, dominating in the polysulfide vulcanizates, may originate

from cyclic sulfides, which are assumed to be frequent in these types of vulcanizates [17]. But they could also be secondary reaction products, as it was shown that thiophenes and carbon disulfide were formed during pyrolysis of a mixture of pure polymer and sulfur or TMTD.

It is evident that different degradation reactions occurs during pyrolysis. These reactions can to some extent be controlled by choosing the appropriate pyrolysis conditions. At e.g. low pyrolysis temperatures (Fig. 2, paper IV) only the B type vulcanizate gave a relatively high yield of carbon disulfide, which could originate from disulfide links and/or from pendent groups. On the other hand at high temperatures high yields of carbon disulfide were obtained for the A type vulcanizate. This could be related to a reaction between sulfur from the polysulfide chains and carbonaceous fragments. At very low temperatures, ca 400°C, degradation reactions yielding mainly nonvolatile products, including elemental sulfur, occurred.

By the method used it was possible to follow the progress of the vulcanization, which was reflected in the product yields. The A system showed a slower vulcanizing process than the B system. This was further indicated by the sulfur content of the samples. It was also possible to study variations between different batches. The variations could be ascribed to varying sulfur content in the original, unvulcanized mixture and to varying efficiency of the curing agents.

For definite qualitative and quantitative determinations of the different types of sulfur bridges it is essential to possess more well defined model compounds than was available for the study in paper IV.

5. PyGC APPLIED TO HYDROCARBONS BONDED TO SILICA GEL

Chemically bonded stationary phases (CBSP) on microporous silica supports have found an increasing use in high performance liquid chromatography (HPLC) [18]. Reversed phase HPLC is the major mode of the technique [19]. The column packing material for the reversed phase HPLC usually consists of normal hydrocarbons bonded to the surface of silica gel. Although reversed phases are a valuable tool, it is also one of the most undefined systems in liquid chromatography [20]. Only very few direct methods have been used for a chemical characterization of these materials [21]. In paper V and VI the application of the PyGC for characterization of reversed phase HPLC stationary phases is presented.

5.1 Pyrolysis conditions

The PyGC studies of the reversed phase packing material were performed employing the pyroprobe. The modified silica (particle diameter 5 μm) is easily blown away and cannot be applied directly on a Pt foil. The probe used consisted of a Pt spiral, in which a quartz tube with a sample holder was introduced

(Fig. 1, paper V). Because of the great mass of the pyrolyzer the temperature rise time was very long and the sample was therefore pyrolyzed during the interval of the rising of the temperature.

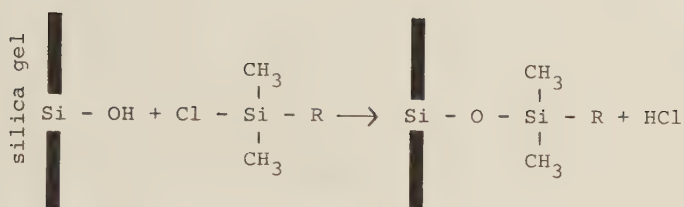
The sample holder was made of a stainless steel net and was remarkably unchanged. The variation in peak height ratios from pyrolysis of test samples were within 10% after half a year.

The pyrolysis temperature was measured with a thermocouple (Fe-Constantan) inserted into the actual sample application part (the bottom of the sample holder). These measurements were performed with the probe removed from the interface. The values of the temperature are therefore somewhat underestimated. A set temperature of e.g. 700°C was measured to 410°C after 5 seconds.

In order to obtain maximum information from the pyrolyses two contradicting demands had to be considered. These are high yields of degradation products and low degree of fragmentation. The choice of pyrolysis conditions must thus be a compromise.

5.2 Characterization

The modified silica gel studied was chemically bonded by different chlorosilanes. For a monofunctional silanizing agent the reaction is illustrated by the following scheme



where R is an hydrocarbon chain. In some of the commercial CBSP alkoxyasilanes were probably used instead of chlorosilanes.

A brief characterization of the CBSP includes determination of the hydrocarbon chain-length and functionality of the silanizing agent.

The pyrolysis products of the hydrocarbon chain were an homologueous series of predominantly monoalkenes. The latest eluted hydrocarbon, which corresponds to the breaking of the Si - C bond in the CBSP, determines the hydrocarbon chain length.

The silanizing agent can be mono-, di- or trifunctional i.e. the agents are either mono-, di- or trichlorosilanes. It is known that the substitution pattern at the silicon atom has a major influence on the bond strength between the silica and the main hydrocarbon chain. Utilizing the peak height ratio between heptadecene (C₁₇) and octadecene (C₁₈) it was possible to differentiate between the three types of silanizing agents (Fig. 2, paper V). A higher functionality yielded a higher C₁₇/C₁₈ peak height ratio (Table III, paper V). It appears that an exchange of Si - CH₃ bonds to Si - O strengthen the Si - C bond of the hydrocarbon chain. This could be attributed to a simple electrostatic effect as the Si - C bond get more of a double bond character, if the silicon atom also is linked to an electrondonner like oxygen.

5.2 Post-silanization

When di- or trichlorosilanes are used as silanizing agents, one must expect unreacted chlorine to remain in the matrix. The bound chlorine can be hydrolyzed to unwanted silanol groups, which can give poor chromatographic performance [22]. Post-silanization (capping) by treating the CBSP with e.g. trimethylchlorosilane (TMCS) will cap residual silanol groups and reduce the negative effects.

It was found that the pyrograms were almost identical for a capped and a noncapped CBSP except for the relative peak height of the methane peak. Several different batches of a commercial CBSP, Nucleosil, were tested as unexpected variations in the LC results were observed. It could be confirmed by the peak height ratio of methane and butene which of the batches that had been capped and thus relate the differences in LC results to capped or noncapped material.

A further study of post-silanization was made in paper IV. Three different capping methods were tested. No appreciable difference in capping efficiency could be noted. Capping by TMCS was preferred because it constitutes the simplest technique.

Capping of mono- and difunctional octadecylsilyl (ODS) bonded silica was also studied. The difunctional ODS-silica was indeed capped by the treatment with TMCS but to a smaller extent than for a threelfunctional. Merely the carbon content from elemental analysis could not detect capping of

difunctional ODS silica. The results from a capped monofunctional ODS silica showed a lower relative methane peak than for a non-capped. This was probably due to a loss of hydrocarbon from the C_{18} chain during the TMCS treatment, which resulted in a lower contribution from the fragmentation of C_{18} chains to the methane peak. Elemental analysis confirmed the loss in carbon content.

5.4 Polymerization

Multifunctional chlorosilanes can, in the presence of traces of water, polymerize [20]. When a monomeric phase is required, the reaction with the silica gel is thus carried out under anhydrous conditions. Commercial and home-made trifunctional ODS phases were tested (Table III, paper V) and variation in the C_{17}/C_{18} peak height ratio was noted. This was believed to depend on the original silica gel and polymerization of the stationary phase. A study of trifunctional ODS bonded to the same silica gel but altered in polymerization is shown in paper VI. It was established that the C_{17}/C_{18} peak height ratio did reflect the degree of polymerization.

Separation of a test mixture by LC on the same trifunctional phases showed no decreased column efficiency for the polymeric ODS phase.

Attempts were also made to polymerize difunctional ODS phases. No major variation in the C_{17}/C_{18} peak height ratio could be observed between the monomeric and polymeric phase. A polymerization limited to the formation of dimeric organosiloxanes was thus suggested.

Few methods are available for the analysis of vulcanized polymeric products and for stationary phases bonded to silica gel. It has been shown in this work, that pyrolysis gas chromatography can provide valuable information about such materials. If the pyrolysis results are correlated to particular properties of the products, the technique could find a broad employment in different technical fields.

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THE INFLUENCE OF THE GAS CHROMATOGRAPHIC AND PYROLYSIS
CONDITIONS ON THE OBTAINED PYROLYSIS RESULTS. EXEMPLIFIED
BY POLYSTYRENE.

Inger Ericsson and Lena Trojer, Department of Analytical Chemistry,
University of Lund, P.O.Box 740, S-220 07 Lund 7, Sweden

Summary

Polystyrenes with different molecular weight, M_w , were pyrolysed at different conditions. The influence of the temperature of the pyrolysis chamber and of the flow rate on the results as well as the influence of the end temperature, the temperature rise time (TRT) and the pyrolysis time was illustrated. Experiments were done to show how the pyrolysis results change during the TRT even if as short as 8 ms. It was demonstrated that much information will be lost if the yields of pyrolysis products are presented as relative values. Differences in results from polystyrenes with different molecular weights were pointed out. The influence of secondary effects on the different pyrolysis products was also studied.

Introduction

The use of pyrolysis as an analytical standard technique requires strict knowledge of the influence of the experimental conditions. This is examined in a project, in which this paper is one part. The temperature before the column, the carrier gas flow and the temperature time profile (TTP) were studied. Earlier the influence of sample size [1], surface area [2] and material of the sample holder [3] have been investigated. Studies were also performed to separate primary and secondary reactions as well as the influence of the molecular weight.

Polystyrene was used as a test substance as its thermal degradation has been thoroughly discussed in the literature. The main objectives have been to use the pyrolysis technique for qualitative and quantitative studies [4-26] and for mechanistic studies of the thermal degradation [6,16,24]. In table I the pyrolysis and gas chromatographic conditions used in some of the papers are given together with the yields, if available, of the styrene monomer, -dimer and -trimer.

Experimental

Apparatus: The pulse pyrolyzer has been described in detail earlier [27]. It consists of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide, which is heated by two current pulses. When not otherwise reported,

the duration of the first pulse is 8 msec. This gives a TRT of 8 msec provided the amplitude of the first pulse is chosen correctly. The pyrolysis temperature is measured by registration of the resistance of the foil and by a temperature calibrated photodiode [2]. The temperature of the pyrolysis chamber was 175°C except for a study of the influence of the chamber temperature when it was set to 115, 145 and 185°C.

GC: Varian 1860

Column: 1.5 m long, 1.9 mm i.d., stainless steel

Stationary phase: 2% Apiezon L on Ultrabond 20 M, 100/120 mesh

Carrier gas: N₂

Flow rates: N₂ - 20 ml/min

H₂ - 20 ml/min

Air - 240 ml/min

Column temperature: Programming 70-250°C, 15°/min

Detector: Flame ionization

Detector temperature: 275°C

Integrator: Varian CDS 101

MS: Finnigan 4021

TGA: Mettler Thermoanalyzer TA-HE-20

Because of the base line drift, during temperature programming, the areas for the peaks with higher numbers than 11 in Fig. 2 were measured manually with an OTT Planimeter. The results were recalculated to the corresponding integrator counts.

The pyrolysis products were identified by a mass spectrometer. A CDS 150 Pyroprobe was used, when the PyGCMS analyses were carried out.

Sample preparation

Polystyrene with narrow molecular weight distributions and with different average molecular weights were used, $\bar{M}_w$: 2100, 20800 and 2610000. These polystyrenes were anionically polymerised (Waters Assoc., Milford, MA, U.S.A.). A technical product of a polystyrene with a broader molecular weight distribution, prepared by radical polymerization (Swedish Polystyrene Factory Ltd, Kävlinge, Sweden) was used as well, $\bar{M}_w$: 260000 - 270000.

The four samples were used when the temperature time profile, TTP I, see Fig. 1, was tested. The other experiments were made with $M_w = 2100$ and $M_w = 2610000$, as $M_w = 20800$ and the technical product behaved like the sample $M_w = 2610000$.

The polystyrenes were dissolved in 2 ml of toluene. The sample, 1 μ l (7.5 μ g), was placed on the middle of the foil with a 1 μ l Hamilton syringe. The solvent was evaporated before pyrolysis.

The amount of sample was chosen to 7.5 μg to get as homogeneous temperature in the sample as possible without increasing the relative amount of catalytic effects excessively [1].

Toluene diluted in carbon disulphide, 1.5 $\mu\text{g}/\mu\text{l}$, was used for the calibration of the detector.

Different temperature time profiles (TTP)

The pyrolysis experiments in this study can be divided into four different modes depending on the TTP. Figure 1 shows the different TTP:s schematically drawn.

- | | |
|---------|---|
| TTP I | Varying end temperatures, the same temperature rise time (TRT) and time enough for complete pyrolysis at the conditions used. |
| TTP II | Varying times and the same temperature change per time unit. |
| TTP III | Varying TRT and the same end temperature. |
| TTP IV | Varying times, the same TRT and end temperature. |

Results

Separation and identification of the pyrolysis products

It is known that polystyrene gives pyrolysis products with a wide range of boiling points. The trimers have boiling points of about 400°C. This makes it necessary to use temperature-programming. A short, low loaded Apiezon L column on an inert support was chosen. It gives a good separation in a short time at a relatively low column temperature and thus the column could be kept low bleeding. The results of the separation and an identification of the products are shown in Fig. 2 D.

Some of the products of low yield have only been characterized by molecular weights or in a molecular weight range.

Precision

The precision in the integrator counts and relative values for the numbered peaks (from Fig. 2) are given in table II.

The results first tabulated are those obtained during four days by two different persons. The pyrolysis conditions were chosen to 750°C and a TRT of 8 ms, the same as the total pyrolysis time. These results can be compared with results obtained during one day and made by one person. Results observed at a high pyrolysis temperature, 1210°C, are also tabulated.

Detector calibration

The detector was calibrated with a toluene solution in order to be able to estimate the amount of high boiling point products (> trimers) kept in the system and thus not detected. The calibration gave $50 \pm 1 \cdot 10^6$ integrator counts (i.c.) per 7.5 µg toluene. With respect to the systematic errors which could occur in the calibration and determination of the peak areas, the interpretation of the total yield could only be a "rough estimation" ($\pm 5\%$). Most of the samples could be accounted for when pyrolyzing samples with M_w between 20800 and 2610000.

Temperature of the pyrolysis chamber and carrier gas flow

The temperature of the pyrolysis chamber affects the pyrolysis results. This is shown in Fig. 2 A, B and D. The temperature was changed from 115 to 175°C. When the temperature was chosen to 185°C a more symmetric peak of the trimer (peak no 15) was obtained without any significant change of the yield.

A low temperature before the column can be compensated for by an increased carrier gas flow, which is shown in Fig. 2 B and C. When the carrier gas flow rate is increased the detector response is changed and the pyrolysis temperature decreases to some extent. However, relative values show that if the carrier gas flow rate was increased the amount of high boiling point components increased, even for those which gave lower yields at lower pyrolysis temperatures.

TTP_I

In Fig. 3 the total yield of pyrolysis products found from the four samples, with different M_w , is plotted against different end temperatures, unfilled signs.

Up to a pyrolysis temperature of about 800°C the total yield of the pyrolysis products increased, almost to the calibrated total yield, for samples with high molecular weights. At highertemperatures the decrease in the total yield of pyrolysis products was drastic.

The total yield of pyrolysis products from the sample of $M_w = 2100$ was considerably lower up to about 800°C than for the samples with higher molecular weights.

The yield of the styrene monomer, expressed in percentage of the total yield of the pyrolysis products, shown in Fig. 4 A, was almost the same for the different molecular weight samples. The yield of styrene expressed as integrator counts, Fig. 4 B, followed the yield of the total amount of products.

In Fig. 5 the yield of the peaks, 1, 3, 11, 12, 14 and 15, are plotted against different end temperatures. From this figure it is obvious that the yield of the dimer, peak no 11, and the trimer, peak no 15, decreased with increasing temperature. The yield of the dimer from the sample of $M_w = 2100$, however, exhibited the same specific behaviour as for its yield of the monomer.

Another noticeable difference in the results between the low molecular weight sample, $M_w = 2100$, and the other three was the amount of low boiling point products, see table IV A and Fig. 5. The yield of low boiling point products was much larger than from the samples with high molecular weights.

TTP II

Two polystyrenes of $M_w = 2100$ and $M_w = 2610000$ were pyrolysed for different times with the same temperature change per time unit up to 1440°C , see Fig. 2, TTP II. These

experiments were done primarily to show what happens with the pyrolysis products during the TRT for a high end temperature. The results can also be compared with those obtained at longer TRT, 8 ms, to temperatures higher than 900°C. The total yield of pyrolysis products, the monomer and some of the other products are presented in the Fig. 3, 6 and 5 respectively, as filled signs.

The results varied in essentially the same way compared to the results from TTP I but with different yields.

TTP III and TGA

Two samples of different molecular weights, $M_w = 2100$ and 2610000, were pyrolysed to an end temperature of 750°C during three different TRT, 8 ms, 108 ms and 1008 ms. The results obtained are seen in table III. The schematic of the TTP used is illustrated in Fig. 1. The results, depending on different TRT, showed no drastig differences.

The two samples were also analysed with thermal gravimetric analyses (TGA). Most of the sample weight decrease (>90%)

occurred during a small temperature interval around 400°C. The behaviour was similar for the two samples. These experiments contributed to the understanding of the results from the different molecular weight samples.

TTP_IV

Table IV A and B show the results from pyrolyses of the two samples, $M_w = 2100$ and $M_w = 2610000$, for different pyrolysis times at two different end temperatures, A 750°C and B 1210°C.

The precision was good enough to show what happened when different pyrolysis times were used. At the lower end temperature, 750°C, the monomer yield was relatively unchanged with time. For the sample $M_w = 2100$ it went through a maximum. Most of the products obtained in small amounts showed an increased yield with time while the yield of e.g. the trimer decreased.

At 1210°C the amount of monomer decreased quite drastically with time while the low boiling compounds, peaks no 1 and 2, and peak no 14 increased. These results can be compared with those obtained when the end temperature increased, Fig. 3, 5, and 6.

Discussion

The influence of the gas chromatographic and pyrolysis conditions on the results obtained cannot be fully understood or explained if the results are presented in relative figures. A lot of information will be lost if only relative results are used. This is shown in Figs. 4 A and B. It is also important to calibrate the detector in order to be able to correlate the total yield of pyrolysis products to the amount of sample pyrolysed.

Gas chromatographic conditions

The influence of gas chromatographic conditions can be of two kinds. Products can condense or be kept in the system and the gas chromatographic conditions can influence the set pyrolysis conditions.

Fig. 2 shows that the temperature of the pyrolysis chamber and the carrier gas flow will influence the pyrolysis results. This means that if the pyrolyzer consists of a chamber with "a small cross-section" e.g. the Curie point pyrolyzer, the carrier gas flow is high and the pyrolysis products are transported on to the column, even if the temperature of the chamber is relatively low.

The kind of carrier gas can e.g. influence the temperature in the sample [28] and may influence the secondary reactions as well.

Secondary effects

A strict definition of primary and secondary reactions or products is difficult to make. In this paper however, a primary reaction has been specified as one which produces a product proportionally to the amount of sample, when pyrolyzed at near ideal pyrolysis conditions. A secondary reaction has been specified as one which yields products even if there is no sample left on the pyrolyzer. Both these two reactions can be checked by experiments.

Primary reactions have earlier been examined [2]. In this paper the results have been focused on the secondary reactions both qualitatively and quantitatively.

When 7.5 μg PS is pyrolysed to an end temperature of 750°C in 8 ms, the sample is nearly totally pyrolysed which is indicated in table III by the rest. The rest is the total yield obtained when the possible sample left is pyrolysed once more at the same pyrolysis conditions. An increase and a decrease of the yield of pyrolysis products at temperatures higher than 750°C and a TRT of 8 msec depends on decomposition of compounds of higher molecular weights to lower. The amount of styrene increased somewhat up to 825°C , probably depending on the decomposition of the dimer, trimer and larger molecules. There is also the possibility of recombination of molecules to a larger product. Peak no 14, a styrene dimer, which area increased to 1300°C (Fig. 5) is an example of a product from a recombination reaction. In Fig. 5 the amount of secondary effects on

some of the peaks can be followed. The mechanisms of secondary reactions are not to be discussed in this paper.

Pyrolysis temperature

When the influence of pyrolysis temperature on the results is presented, mostly the pyrolysis time is kept constant and nothing is said about changes in the TRT. It is well known that at high temperatures the degradation is complete before the end temperature is even reached [29], assuming a small sample size.

The increase of the total yield of pyrolysis products (Fig. 3) up to 800°C is explained by the degradation of high boiling points products (>trimers). The large difference in results at low temperatures between the sample of $M_w = 2100$ and the other three samples of $M_w = 20800 - 2610000$ are certainly depending on the competition between the volatilization and decomposition of low molecular weight species or of molecules which have only been partly degraded. This will be further discussed below.

At high temperatures the decrease of the total yield of pyrolysis products is attributed to carbonization. This was verified by a black residue on the platinum foil and also by the results obtained from the TTP II. Carbonization was also obtained at pyrolysis of polybutadiene [2].

TRT

The expected effects of long TRT:s are that a larger part of the sample is degraded at lower temperatures and that chances for secondary reactions are increased depending on the longer pyrolysis time.

In table III it is seen that the yields at the longest TRT, 1000 ms, are mostly affected by differences in the temperature. This conclusion is drawn by studying the change and amount of low boiling point products as well as the trimer. A decrease of the temperature will influence the results by decreasing the yield of low-boiling point products, Fig. 5, and of the monomer, Fig. 6, and by increasing the yield of the trimer, fig. 5. Secondary effects however, will be influenced in the opposite way, table IV A.

For the sample of $M_w = 2100$ the influence of a longer TRT will be noticed principally as secondary effects. The origin of the increase of the monomer is a decomposition of high boiling point products, which are not passing the gas chromatographic system.

At temperatures higher than 800°C the influence of the TRT on the results was more obvious, fig. 3. A difference of the TRT of a few ms to the same end temperature markedly influenced the total yield, especially for the high molecular sample, $M_w = 2610000$.

The differences in the results between the two samples of $M_w = 2100$ and $M_w = 2610000$ could be explained by the differences in the primary pyrolysis products formed. The high molecular weight sample initially gives much more monomer and less high boiling point products than the low molecular weight sample.

At a high pyrolysis temperature the reaction rates are very high, which means that the pyrolysis times can have a strong influence even if the difference is only a few milliseconds. A shorter time means less secondary reactions, i.e. carbonization in the case of high molecular weight sample and degradation of high boiling point products in the case of the low molecular weight sample.

Time

Usually excessive pyrolysis times are chosen in order to guarantee that the sample is totally pyrolysed. The fact that secondary effects will influence the results is often neglected.

When the two polystyrenes are pyrolysed to two different end temperatures the secondary effects can be followed in table IV, A and B. It is possible to discriminate between products decomposed and formed by secondary reactions. The influence of the pyrolysis time is much more evident at the high pyrolysis temperature 1210°C for the two samples.

The change of the amount of pyrolysis products per time unit decrease with time as the primary products escape from the hot metal foil. A maximum of the yield of the pyrolysis products is seen for the sample, $M_w = 2100$ again depending on the contribution of products degraded from the high boiling point products. Carbonization will influence more than formation at longer times.

Influence of the molecular weight

A large difference in the results between the low molecular weight sample, $M_w = 2100$, and the samples with molecular weights of 20800 and higher was obtained, Fig. 3,5,6.

When a molecule is degraded it is supposed that the formation of styrene takes place by unzipping. Before the molecule is totally degraded there is one part of the molecule which is exposed to volatilization. The difference in results must therefore depend on the number of end points for the different samples.

From the literature [30] it is found that for a polystyrene molecule with less than nine monomers, vaporization prevail over decomposition. The number must be dependent on the pyrolysis conditions used. In Fig. 6, at the lowest temperature the results seem to be in agreement but when the temperature increases the number of monomers in the part of the molecule left for volatilization decrease.

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TABLE I. Conditions used and results obtained by different authors when pyrolysing polystyrene of varying molecular weights.

Year	Authors	Sample		Pyrolysis Conditions			
		Ref	Molecular weight	Amount	Apparatus	Temp /°C	Time /s
1968	P.Fuchs et al	4		0.1 mg	filament		0-15
1969	C.E.R.Jones et al	5		4 µg	- " -	700	
1969	H.McCormick	6		5-10 µg	- " -	250-500	10
1968	F.Sonntag	7		1.4 µg	- " -	900	
1975	N.B.Zaitsev et al	8	440000 ¹	40 µg	- " -	380-514	
1976	G.Oehme	9			Curie-point	800	4
1977	K.G.Häusler et al	10		30-50 µg	- " -	600	4
1969	O.F.Folmer Jr et al	11			laser		0.4x10 ⁻³
1961	F.Lehmann et al	12	233000 ²	2-3 mg	coil	425-1125	5-30
1974	N.Iglauer et al	13		2-5 mg	- " -	1000	10
1967	G.J.Knight	14		1-5 µg 1-3 mg	oven	600-700	
1966	T.A.Turner et al	15	20000- 230000	1-1.2 mg	- " -	850,980	
1967	D.Noffz et al	16		200 µg	Curie-point	768	2
1969	T.Tsuge et al	17	9000- 1800000 ²	0.25 mg	oven	515-650	60
1978	P.Gambert et al	18	500000	1 µg	ribbon	1000	20x10 ⁻³
1976	C.N.Cascaval et al	19	2450- 125000 ²	0.6 mg	ribbon	660	10
1976	J.P.Schmid et al	20		1 µg	Curie-point	760	10
1977	S.Tsuge et al	21		0.05-0.5 mg	oven	510	
1975	P.Vermande et al	22	418000 ³	15 g	oven	515-820	900
1978	Y.Sugimura et al	23	1800000 ³	30-200 µg	oven	490	
1968	H.D.R.Schüddemage et al	24		0.2-0.5 mg	coil	<350	
1977	P.P.Schmid et al	25		0.1-1 µg	Curie-point		0.5
1973	S.G.Coloff et al	26	230000		laser	800	0.1
1980	Present work		2100- 2610000 ³	7.5 µg	ribbon	630	0.35

1. M_v

2. M_n

3. M_w

* Related to a detector calibrated value

GC-conditions (if not PyMS is used)					Result: Yields/%		
RT s	Interface temp/°C	Stationary phase	Column length/m	Column temp/°C	Monomer	Dimer	Trimer
.48- .56		10% Apiezon L	2	140	97.3		
		10% Ethyleneglycole distearate	1.4	85	100		
		20% Polyester (DEGS)	2	temp progr	49		
		5% SE 30	1.5	85	69 *		
		10% Polyethylene glycole adipat	1.2	90	100		
		2% Fluhyzon	3	60-180, 3/min	x		
-15		Squalane	120	20	73		
		20% SE 52	1.8	70-250, 24/min	x		
		30% Apiezon L	1.8	140	62.8-83.9		
		30% Chlorowax 70	1.8	140			
		Silica gel	1.8	100			
		10% SE 30		50-250, 10/min	x		
.05	150	20% Silicone grease		150	63-100*		
		30% Apiezon L	1.8	160	55-88		
		Polyphenylether OS124	100	60-200, 5/min	x *	x	
.013		10% Apiezon L	2	50-250, 20/min	65.5-86.8 *	4.4-12.7 *	
		mass			x	x	
		10% Apiezon L	1.8	80-230, 16/min	42.8-51.6	15.8-25.9	13.4-16.2
.15 .8		SE 52	20	25-250, 6/min	x	x	x
		5% FFAP	2	50-260, 12/min	x	x	x
		10% Carbowax 20 M			74-80	3-10	x
		5% OV-101	1	50-300, 10/min	77	8.7	14.3
		mass			x	x	x
		mass			x	x	x
		mass			x	x	x
		2% Apiezon L	1.5	70-250, 15/min	50-85 *	1.6-2.9*	1.6-3.3 *

TABLE II

The precision in results obtained from the pyrolysis products presented in Fig. 2 D.

Peak no	1	2	3	4	5	6	7	8	9	10	11	12*	13*	14*	15*	Total counts
4 days, n = 9, 2 persons, PS 2 610 000, 750°C, 8 ms																
$\bar{x}_A \times 10^{-6}$	0.018	0.022	0.32	0.040	44.6	0.095	0.19	0.050	0.46	0.28	1.37	0.24	0.31	0.34	1.2	50.8
S_A	17	8.6	3.4	12	1.7	7.6	4.9	15	5.5	8.4	3.9	7.7	12	14	17	1.9
$\bar{x}_R$	0.035	0.043	0.64	0.079	87.9	0.19	0.38	0.098	0.91	0.55	2.7	0.48	0.62	0.68	2.4	
S_R	15	7.8	3.3	11	0.60	8.4	4.7	14	4.3	7.5	2.5	7.6	11	13	16	
1 day, n = 3, 1 person, PS 2 610 000, 750°C, 8 ms																
$\bar{x}_A \times 10^{-6}$	0.015	0.022	0.31	0.038	43.7	0.094	0.19	0.040	0.44	0.28	1.29	0.24	0.27	0.30	1.06	49.3
S_A	3.3	3.4	1.1	8.2	1.9	11	2.3	1.5	1.6	3.7	4.2	7.7	4.0	12	11	2.2
$\bar{x}_R$	0.030	0.044	0.64	0.077	88.6	0.19	0.38	0.082	0.90	0.57	2.62	0.49	0.54	0.61	2.1	
S_R	4.2	5.0	2.3	9.8	0.40	10	0.15	1.8	0.61	5.4	1.9	6.7	6.1	13	9.1	
1 day, n = 3, 1 person, PS 2 100, 1210°C, 8 ms																
$\bar{x}_A \times 10^{-6}$	2.11	2.3	1.28	0.24	20.8	0.26	0.31	0.74	0.67		0.25	0.92		0.49	0.11	33.2
S_A	3.2	7.7	2.8	6.1	3.7	9.1	4.9	4.2	3.8		10	2.3		2.2	10	3.2
$\bar{x}_R$	6.4	6.9	3.9	0.72	62.8	0.78	0.94	2.24	2.0		0.74	2.77		1.48	0.32	
S_R	4.4	9.1	3.4	2.9	1.0	6.3	1.6	0.9	6.8		7.3	3.4		1.4	8.5	

$\bar{x}_A$, $\bar{x}_R$ = mean value calculated on the absolute and relative ingratator counts, respectively.

S_A , S_R = standard deviation in percent of the mean value calculated on the absolute and relative ingratator counts, respectively.

* = values calculated on planimeter areas converted to integrator counts.

The influence of the temperature rise time to an end temperature of 750°C (TTP III) . The results are given in integrator counts x 10⁻⁶. Peak number see Fig. 2 D.

Peak no	1	2	3	4	5	6	7	8	9	10	11	12*	13*	14*	15*	Total counts	Rest
PS 2 610 000																	
8	0.021	0.025	0.31	0.045	44.6	0.103	0.20	0.066	0.50	0.32	1.41	0.26	0.22	0.39	1.1	50.9	0.084
108	0.043	0.050	0.40	0.076	44.9	0.084	0.34	0.185	0.70	0.50	1.71	0.34	0.22	0.56	0.71	52.0	0.007
1008	0.026	0.030	0.38	0.029	42.3	0.022	0.24	0.107	0.48	0.18	1.73	0.26	0.34	0.39	1.8	49.3	0.002
PS 2 100																	
8	0.46	0.046	0.50	0.086	24.1	0.30	0.17	0.093	0.59	0.36	0.95	0.26	0.43	0.17	0.76	30.7	0.48
108	0.59	0.081	0.57	0.119	26.7	0.37	0.31	0.22	0.82	0.44	1.26	0.39	0.35	0.26	0.56	34.8	0.072
1008	0.41	0.048	0.62	0.077	28.5	0.20	0.22	0.14	0.55	0.23	1.03	0.24	0.32	0.17	1.1	35.3	0.005

* = planimeter areas converted to integrator counts

Rest indicates what is left after one pyrolysis.

TABLE IV A

The influence of the pyrolysis time (TPT not included) at the pyrolysis end temperature 750°C.
The results are given in integrator counts $\times 10^{-6}$. Peak numbers see Fig. 2 D.

Peak no	1	2	3	4	5	6	7	8	9	10	11	12*	13*	14*	15*	Total counts
t/ms																
PS 2 610 000																
0	0.016	0.024	0.31	0.040	43.4	0.095	0.20	0.057	0.45	0.28	1.20	0.24	0.23	0.30	0.99	48.7
10	0.022	0.027	0.31	0.044	43.4	0.111	0.21	0.072	0.50	0.36	1.31	0.26	0.21	0.36	0.72	48.9
20	0.023	0.030	0.31	0.048	43.4	0.108	0.23	0.096	0.54	0.40	1.35	0.25	0.21	0.40	0.56	48.9
50	0.029	0.037	0.33	0.059	43.5	0.108	0.27	0.143	0.60	0.43	1.40	0.28	0.16	0.37	0.49	49.2
200	0.048	0.061	0.37	0.081	44.1	0.112	0.35	0.195	0.71	0.41	1.44	0.27	0.12	0.41	0.39	49.0
1000	0.066	0.079	0.38	0.098	44.8	0.117	0.37	0.284	0.76	0.38	1.34	0.35	0.12	0.37	0.41	51.1
5000	0.094	0.099	0.40	0.112	43.8	0.105	0.39	0.363	0.81	0.34	1.22	0.35	0.08	0.31	0.31	51.9
PS 2 100																
0	0.44	0.040	0.47	0.084	22.1	0.26	0.15	0.030	0.53	0.28	0.67	0.21	0.30	0.13	0.48	27.1
10	0.48	0.051	0.46	0.090	23.6	0.31	0.18	0.049	0.60	0.35	0.80	0.19	0.25	0.13	0.37	28.9
20	0.49	0.054	0.46	0.089	28.6	0.33	0.20	0.106	0.62	0.40	0.87	0.24	0.26	0.16	0.37	34.2
50	0.54	0.068	0.49	0.105	26.0	0.35	0.25	0.151	0.70	0.44	0.96	0.32	0.28	0.21	0.34	32.4
200	0.62	0.097	0.53	0.129	27.0	0.38	0.32	0.195	0.82	0.47	0.96	0.32	0.22	0.28	0.30	33.8
1000	0.67	0.124	0.53	0.151	26.6	0.39	0.36	0.282	0.89	0.43	0.86	0.37	0.19	0.19	0.22	33.5
5000	0.71	0.142	0.56	0.174	25.0	0.37	0.39	0.377	0.94	0.38	0.80	0.39	0.15	0.17	0.17	31.9

* = planimeter areas converted to integrator counts

The influence of the pyrolysis time (TPT not included) at the pyrolysis end temperature 1210°C.

The results are given in integrator counts $\times 10^{-6}$. Peak number see Fig. 2 D.

t/ms	Peak no	1	2	3	4	5	6	7	8	9	10	11	12 *	13*	14*	15 *	Total counts
PS 2 610 000																	
0	1.47	3.0	1.01	1.02	24.1	0.027	0.22	0.51	0.42			0.173	0.93		0.73	0.07	35.5
10	1.93	4.1	0.99	0.89	22.0	0.016	0.19	0.52	0.39			0.144	0.76		0.93	0.09	35.2
20	2.03	4.3	0.88	0.83	20.1	0.018	0.16	0.48	0.37			0.161	0.62		0.95	0.09	32.4
50	2.36	4.9	0.79	0.70	17.1	0.011	0.13	0.42	0.34			0.117	0.56		0.93	0.07	30.6
200	2.25	4.6	0.64	0.53	13.1		0.09	0.34	0.30			0.077	0.41		0.86	0.07	25.0
5000	4.05	7.0	0.59	0.37	8.0		0.04	0.41	0.37			0.018	0.30		1.1		24.4
PS 2 100																	
0	2.11	2.3	1.28	0.24	20.8	0.26	0.31	0.74	0.67			0.25	0.92		0.49	0.11	33.2
10	2.47	3.1	1.28	0.20	18.3	0.21	0.27	0.73	0.63			0.21	0.76		0.63	0.06	31.7
20	2.72	3.6	1.36	0.21	23.4	0.20	0.26	0.88	0.62			0.20	0.76		0.75	0.11	38.2
50	3.23	4.5	1.33	0.19	21.8	0.18	0.23	0.88	0.60			0.18	0.69		0.82	0.06	37.9
200	3.52	4.9	1.14	0.14	17.4	0.11	0.16	0.77	0.52			0.13	0.58		0.86	0.07	33.0
5000	5.55	7.4	0.97	0.08	10.4	0.03	0.07	0.71	0.48			0.02	0.34		1.02		30.1

* = planimeter areas converted to integrator counts

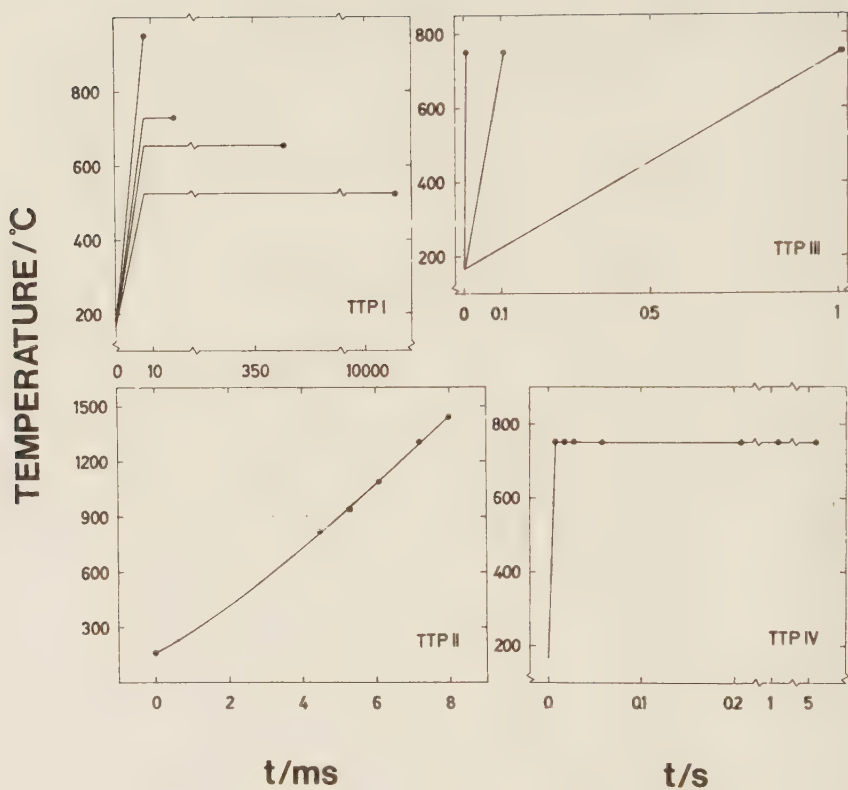


Fig. 1. Schematics of the different temperature time profiles (TTP) used for the experiments in this investigation. The points show the pyrolysis conditions used. For TTP I the pyrolysis time was 8 msec at temperatures above 800°C.

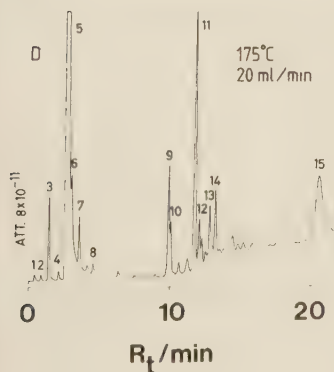
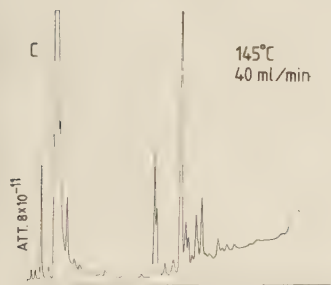
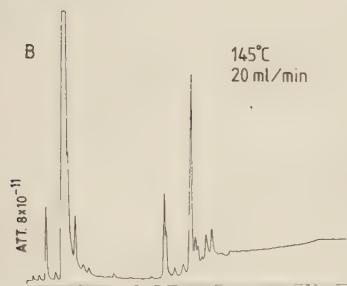
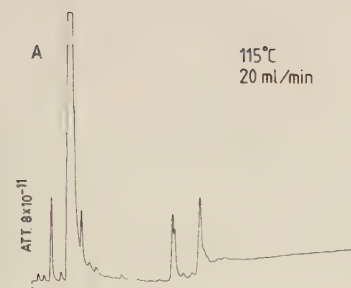


Fig. 2. Pyrograms obtained at different temperatures of the pyrolysis chamber and carrier gas flows, when 7.5 g PS M_w 2610000 was pyrolysed to an end temperature of 750°C reached in 8 msec. Peak no:

1. $C_1 - C_5$ 2. benzene
3. toluene 4. ethylbenzene
5. styrene 6. M_w 118
7. M_w 118 8. M_w 116
9. M_w 182 11,12. M_w 208 (dimer)
- 13,14. M_w 208-230
15. M_w 312 (trimer)

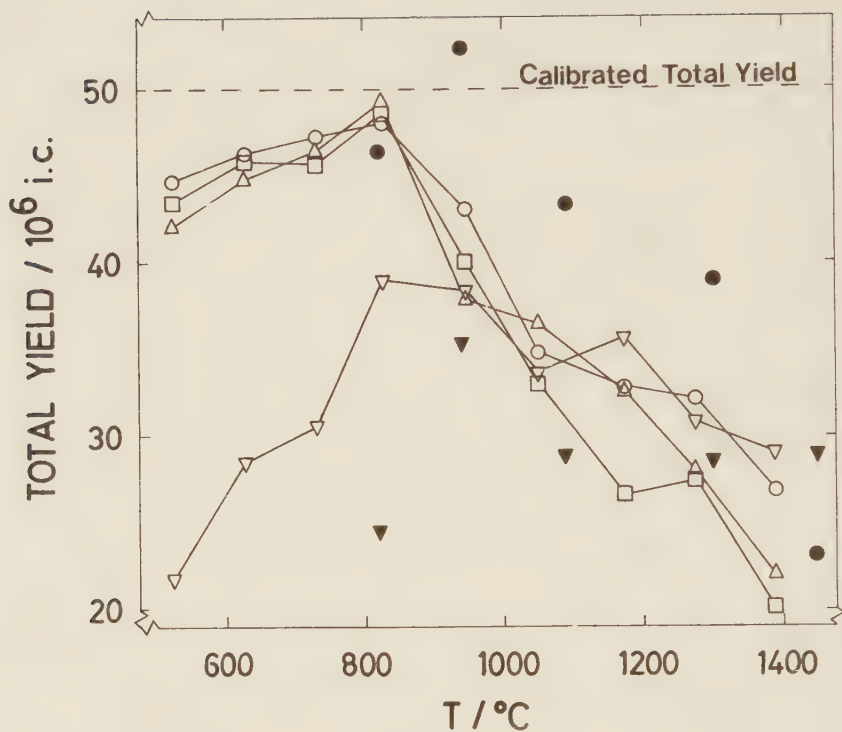


Fig. 3. The total yield of the pyrolysis products versus the pyrolysis end temperatures, i.c. = integrator counts.

POLYSTYRENE

TTP I

TTP II

M_w 2 610 000

○

●

20 800

△

▲

2 100

▽

▼

Technical product

□

■

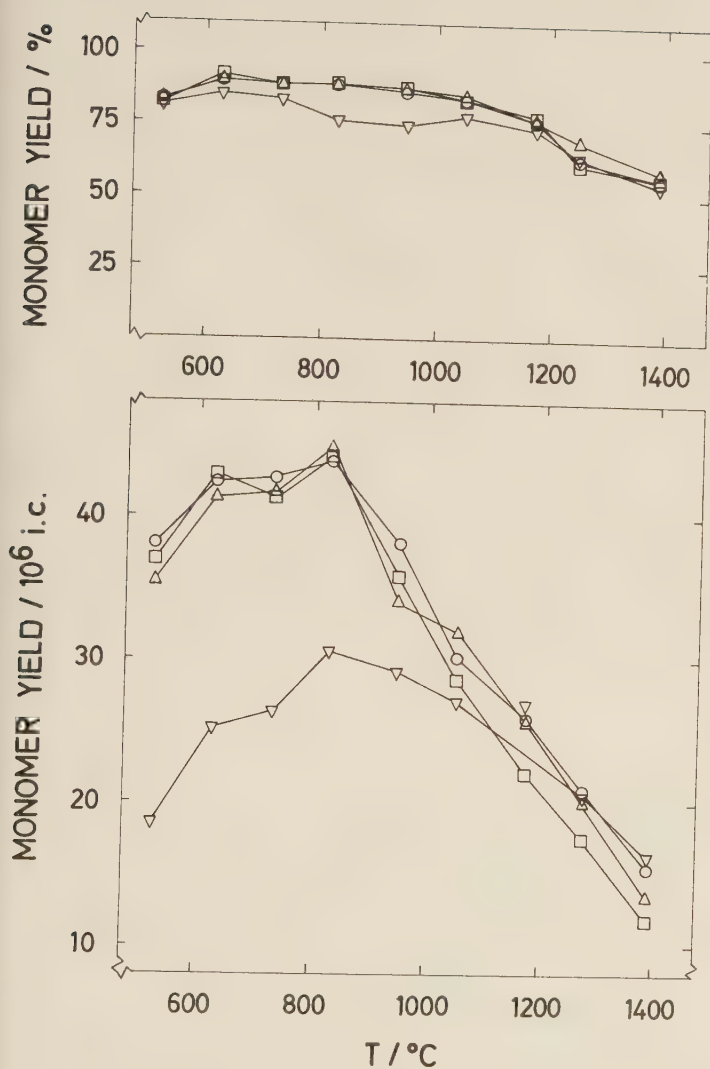


Fig. 4A (above): The yield of the styrene monomer expressed as percentage of the total yield of the pyrolysis products versus the pyrolysis end temperatures (TTP I) for the four different polystyrenes.

4B (below): The yield of the styrene monomer expressed as integrator counts versus the pyrolysis end temperatures from the same experimental results as in Fig. 4 A.

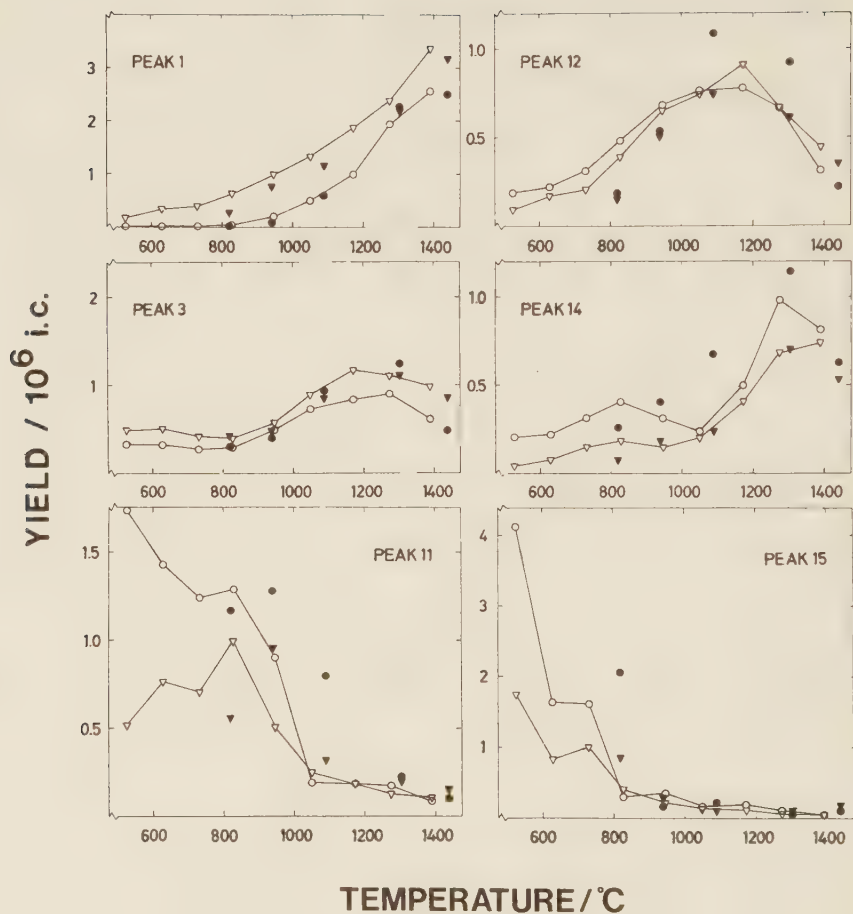


Fig. 5. The yield of some of the pyrolysis products versus the pyrolysis end temperatures, i.c. = integrator counts.

POLYSTYRENE

M_w 2 610 000

2 100

TTP I



TTP II



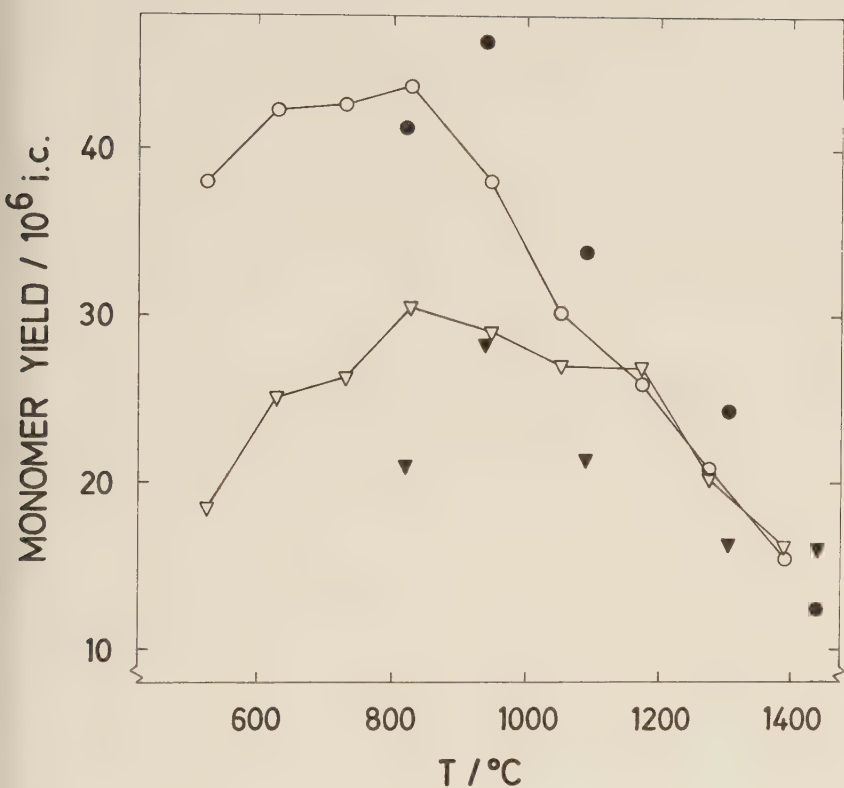


Fig. 6. The yield of the styrene monomer versus the pyrolysis end temperatures, i.c. = integrator counts

POLYSTYRENE

TTP I

TTP II

M_w 2 610 000

$\circ$

$\bullet$

2 100

∇

$\blacktriangledown$

HYDROGEN FORMATION DURING PYROLYSIS OF POLYSTYRENE

LENA TROJER

*Department of Analytical Chemistry, University of Lund, P.O. Box 740,
S-220 07 Lund 7 (Sweden)*

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SUMMARY

Hydrogen was identified as a product of the pyrolysis of polystyrene, especially at high pyrolysis temperatures. With a high interface temperature of the Pyroprobe foil pyrolyser and a high pyrolysis temperature, almost 100% of the pyrolysed polymer could be accounted for. It is then assumed that hydrogen (up to 26%) produces a corresponding amount of carbon, which remains on the foil.

INTRODUCTION

Carbon residues have been observed on the sample holder [1] during the pyrolysis of polystyrene at high temperatures (above 1200°C). A foil pulse pyrolyser [2] was used during these experiments. It is reasonable to expect carbonization to some extent also at lower temperatures, and for polybutadiene [3] carbonization has been observed even at 500°C. The formation of carbon from organic compounds should result in the production of hydrogen or hydrogen-rich compounds as the carbon residue can be expected to have a lower hydrogen to carbon ratio than the parent compound.

This study was carried out in order to investigate the hydrogen formation and to see if the formation of carbon and hydrogen could account for the difference in the expected and obtained yields of hydrocarbon pyrolysis products. The hydrogen produced under various pyrolysis conditions was measured with a thermal conductivity detector. Any amount of hydrogen detected will indicate that a corresponding amount of carbon remains on the sample holder.

EXPERIMENTAL

Apparatus

A CDS 150 Pyroprobe with a 38 mm long and 1.6 mm wide platinum foil was used. The pyrolyser was mounted directly on the injection port of the gas

chromatograph. The interface temperature was normally set at 115°C but in some instances 250°C was used. After the measurements had been made it was found that the timer calibration was erroneous, a set time of 20 s corresponding to 25 s. It is not known if this error had been present all the time and the times reported are 20% low.

The hydrogen formation was measured with a Varian 3700 gas chromatograph with a thermal conductivity detector (TCD). The peak area was evaluated with a planimeter.

The hydrocarbon pyrolysis products were studied using a Varian 1860 gas chromatograph with a flame-ionization detector (FID). The peak areas were measured with a Varian CDS 101 electronic integrator.

For the TCD measurements it was necessary to dry the carrier gas with a drying tube (Anhydrone filter; Varian), otherwise water would decompose, resulting in a peak when an empty ribbon was pyrolysed.

Chromatographic conditions

Thermal conductivity detector

Column: 2-m Chromosorb 102 with a daily exchanged 0.1-m pre-column packed with the same adsorption material. Column temperature: 40°C. Carrier gas (nitrogen) flow-rate: 20 ml/min. Detector temperature: 100°C. Detector filament temperature: 170°C.

Flame-ionization detector

Column: 2-m 5% FFAP on Chromosorb W AW DMCS, 80–100 mesh. Column temperature: programmed from 50 to 250°C at 12°C/min. Carrier gas (nitrogen) flow-rate: 20 ml/min. Hydrogen flow-rate: 20 ml/min. Air flow-rate: 240 ml/min. Detector temperature: 275°C.

Sample preparation

The polystyrene was anionically polymerized (Waters Assoc., Milford, MA, U.S.A.), with an average molecular weight of 2,610,000. The polystyrene (15 mg) was dissolved in 2 ml of toluene. The sample (1 μ l) (7.5 μ g of polystyrene) was placed on the platinum ribbon. The solvent was evaporated before pyrolysis.

The FID was calibrated by the injection of carbon disulphide solutions of toluene or styrene. As the FID response was the same for styrene and toluene, toluene was normally used in the calibration. The response factors for the other pyrolysis products were identical with that of styrene to within 10%. As styrene accounted for 90% of the pyrolysis products, the total calibration should be of acceptable accuracy with toluene as a standard throughout.

The TCD was calibrated with 50–200 μ l of mixtures of 0.5% and 1.0% hydrogen in nitrogen (S.T.P.).

RESULTS AND DISCUSSION

Hydrogen as a product of the pyrolysis of polystyrene was identified by comparing the retention times with those of standards under gas chromatographic conditions such that hydrogen, air and methane were separated.

Hydrogen formation was observed at pyrolysis temperatures between 510 and 980°C. The yield of hydrogen increased with increasing temperature, as illustrated in Fig. 1. The pyrolysis times were 5 s, except at 510°C, where it was necessary to use a pyrolysis time of 20 s for complete pyrolysis.

The formation of hydrogen as a function of pyrolysis time was also studied. The results are given in Fig. 2. The hydrogen yield increased considerably with increasing pyrolysis time.

The increase in the hydrogen yield with increasing pyrolysis times was unexpected, as the carrier gas flow during 5 s corresponds to the pyrolysis chamber volume. The decomposition of the sample should be complete within less than 1 s (cf., ref. 1, Fig. 4).

The same result of increasing hydrogen yield with increasing pyrolysis temperature and pyrolysis time was obtained at a nominal interface temperature of 250°C, although with even higher hydrogen yields.

Fig. 3 shows the variation of the total yield of hydrocarbons with pyrolysis temperature. The yield was almost constant up to about 800°C. The yield was at most 88% of the value expected if only hydrocarbons had been formed. The reproducibility of the total yield was within 5% expressed as relative standard deviation and measured at 610, 770 and 980°C with pyrolysis times of 10 and 20 s.

Styrene trimer was observed only at a pyrolysis temperature of 510°C with the nominal interface temperature at 115°C. Its contribution corresponded to 3% of the total yield of hydrocarbons. At the highest nominal interface temperature the yield of trimer corresponded to 3, 1.5 and <1% at 610, 770 and 980°C, respectively, and a 5-s pyrolysis time. At 510°C and

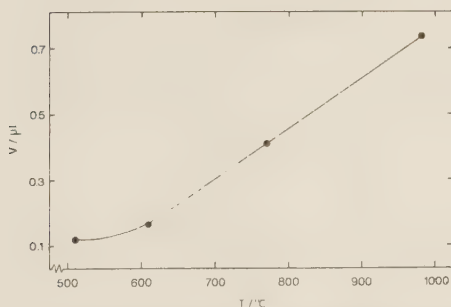


Fig. 1. Volume of hydrogen (S.T.P.) formed at different pyrolysis temperatures. Pyrolysis times: 5 s at 610, 770 and 980°C, 20 s at 510°C.

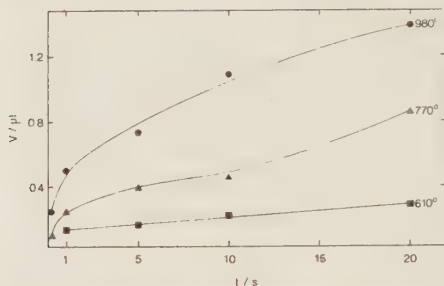


Fig. 2. Volume of hydrogen (S.T.P.) formed at different pyrolysis times.

a 20-s pyrolysis time the yield of trimer was 8%. The reproducibility of the trimer peak was rather low (ca. 50%).

Styrene trimer is the highest molecular weight product observed in more than trace amounts [4-7] in the pyrolysis of polystyrene. The low yield of trimer at the lower interface temperature indicates condensation of the trimer and possibly higher oligomers and other products on the walls of the pyrolysis chamber.

Fig. 4 shows that the total hydrocarbon yield decreased with longer pyrolysis times at 770°C and 980°C. The hydrocarbon decreased to the same extent as the hydrogen yield increased (see Table 1). At 610°C the hydrocarbon yield was constant, whereas the hydrogen yield (Fig. 2) increased with increase in the pyrolysis time.

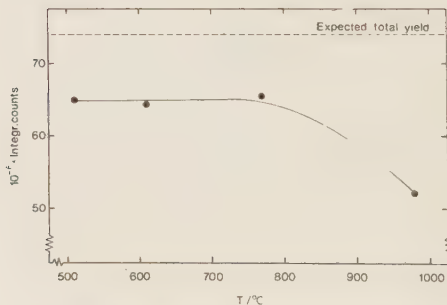


Fig. 3. Integrator readings summed over all the hydrocarbon pyrolysis products as a function of the pyrolysis temperature. Pyrolysis times: 5 s at 610, 770 and 980°C, 20 s at 510°C.

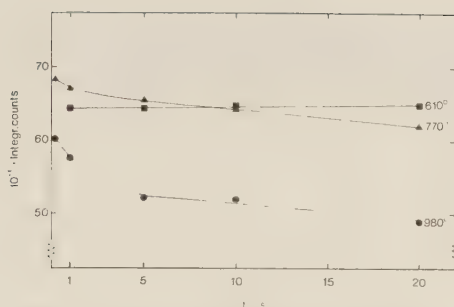


Fig. 4. Total integrator reading for all the hydrocarbon pyrolysis products as a function of pyrolysis time.

The results can be explained if it is assumed that high molecular weight species are primarily produced and if these are decomposed to a substantial extent with increasing foil temperature and time. These species will condense with a short pyrolysis time, a low pyrolysis temperature and a low interface temperature, and escape detection. The primary products were exposed to secondary effects (see Figs. 2 and 4) even after 10 s, owing to circulation of the carrier gas so that products are transported to the heated foil in a com-

TABLE 1

Relative total yield of the hydrocarbon pyrolysis products, relative hydrogen yield and the sum of the two for an interface temperature of 115°C

The total yield from the FID is expressed as a percentage of the value expected if 7.5 μg of polystyrene had been converted entirely to hydrocarbons. The hydrogen yield is expressed as percentage of the value expected if all hydrogen in 7.5 μg of polystyrene had been available as free hydrogen.

Temperature (°C)	Time (s)	FID total yield (%)	TCD hydrogen yield (%)	Total FID + TCD yield (%)
610	1	86.9	1.4	88.3
	5	86.9	1.8	88.7
	10	87.4	2.6	90.0
	20	87.6	3.6	91.2
770	0.2	92.3	0.8	93.1
	1	90.7	2.9	93.6
	5	88.6	4.8	93.4
	10	86.8	5.9	92.7
980	20	83.8	11.4	95.2
	0.2	81.4	3.7	85.1
	1	77.8	7.9	85.7
	5	70.5	11.4	81.9
	10	70.1	14.7	84.8
	20	66.2	18.8	85.0

TABLE 2

Relative total yield of the hydrocarbon pyrolysis products, relative hydrogen yield and the sum of the two for an interface temperature of 250°C

Temperature (°C)	Time (s)	FID total yield (%)	TCD hydrogen yield (%)	Total FID + TCD yield (%)
510	20	83		
610	10	86	4	90
770	5	87	10	97
980	5	80	14	94
	10	80	19	99
	20	72	26	98

plex way, giving rise to secondary effects, especially at high temperatures.

The results are summarized in Tables 1 and 2. The results are not directly comparable as it has been shown [8] that an increased interface temperature increases the pyrolysis temperature. It can be seen that more hydrogen is produced at the higher interface temperature. The total yield was also higher, and approached the theoretical value when both the pyrolysis time and temperature were high.

At a low interface temperature, on the other hand, there is condensation throughout and therefore the total yield will be less than 100%. The yield of hydrocarbon is the same independent of the interface temperature, except at 980°C. At a low interface temperature some hydrocarbons escape detection owing to condensation, and at a high interface temperature the losses will be due to increased formation of carbon and hydrogen. The constancy of the hydrocarbon yield is thus coincidental.

The overall conclusions are that a considerable fraction of the polymer is degraded in such a way that hydrogen is produced. The amount of hydrogen is large at high pyrolysis temperatures. This supports conclusions drawn earlier about degradation to carbon and hydrogen [1,3].

ACKNOWLEDGEMENTS

I thank Dr. Lars Haraldsson and Professor Gillis Johansson for valuable discussions and linguistic help.

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Pyrolysis Gas Chromatography Studies of Insoluble Samples. Exemplified by Vulcanized Styrene Butadiene Rubber

Lena Trojer and Inger Ericsson, Department of Analytical Chemistry, University of Lund, P.O. Box 740 S-220 07 Lund, Sweden

Abstract

A foil pulse pyrolyzer was used for analysis of insoluble samples. The sample size, the pyrolysis temperature, and the pyrolysis time were varied. It was possible to make quantitative determinations of the polymer using unvulcanized copolymers as standard substances. The relative standard deviation of the main peak was 1%. The amount of residue was determined and related to carbon black and zinc oxide in the sample and the influence of the sulphur content in the vulcanized rubber was studied.

Introduction

Pyrolysis gas chromatography (PGC) under well defined and reproducible conditions is a useful technique for analysis

of polymers. A general opinion is that the continuous mode units seem to be more suitable than the pulse mode units when pyrolysing insoluble samples (1,2). Most work on pyrolysis of insoluble samples has been done on vulcanized rubber (3-14). The samples have been analyzed for the polymer - directly (3, 6, 7, 10-13, 15, 16) and after chemical pretreatment (4, 5, 8, 9) - or for the carbon black residue (14). Table I summarizes results reported in the literature.

The aim of this work was to decrease the sample size and optimize the pyrolysis conditions in order to improve the precision. With a good precision of the pyrolysis results quantitative analysis of the polymer can be performed, and differences depending on the sulphur content can be observed.

Table I. Pyrolysis Conditions Used and Results Obtained by Different Authors When Pyrolysing Insoluble Samples

Publ. year	Author	Reference	Type of pyrolyzer	Sample amount/ mg	Pyrolysis temp/°C	Pyrolysis time/s	Relative standard deviation/%	Total analysis time*
1964	B. Groten	3	Continuous mode unit	1	950	26		<1 hr
1972	A. Krishen	4	Continuous mode unit	0.5-0.8	700	30	(3.2)	~10 hr
1974	A. Krishen, et al.	5	Modified Curie point	0.5-0.7	770	15	(1.5)	~6 hr
1969	Y. Namiki, et al.	6	Continuous mode unit	1	560		3	20 min
1970	I.L. Eventova, et al.	7	Continuous mode unit		900			
1971	F. Armitage	15	Continuous mode unit	1-2	620	20	6	~30 min
1968	D.A. McKillop	8	(Pyrolysis-IR)	1000	390	600	4	night + ~1 hr
1970	W. Mills, et al.	9	(Pyrolysis-IR)	200-300	900	10	4	night + ~3 hr
1972	T. Okumoto, et al.	14	DTA, furnace					~2 hr
1969	A.A. Foxton, et al.	10	Wire pulse pyrolyzer	0.4-0.6	750	15		
1977	J. Hu	13	Wire pulse pyrolyzer		1000	15		
1970	G.L. Coulter, et al.	11	Modified Curie point	0.3-0.6	610	10		15 min + weighing
1977	G.L. Coulter, et al.	12	Modified Curie point	0.5	770			30 min
1974	P. Cukor, et al.	16	CDS pyroprobe	0.5				
1978	Present work		Foil pulse pyrolyzer	0.05-0.1	900	1.0	0.80 (0.75)	20 min
				0.2-0.3	900	1.2	0.9 (1.1)	

Values in brackets are calculated from relative values.

* Briefly estimated.

Experimental

Apparatus and GC Conditions.

The pulse pyrolyzer has been described in detail in an earlier paper (17). The pyrolyzer consisted of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide. It was heated by two current pulses. The duration of the first pulse was 8 msec, which gives a temperature rise time (TRT) of 8 msec, provided the amplitude of the first pulse is chosen correctly. The pyrolysis temperature was measured by registration of the resistance change of the foil and by a temperature calibrated photodiode (18).

The pyrolyzer was linked to a 3 m long stainless steel column containing 15% Apiezon L on Chromosorb W, AW, DMCS, 80/100 mesh. The temperature was 150°C at isothermal conditions, and 50-175°C at temperature programming with a heating rate of 10°C per minute. The temperature of the pyrolysis chamber was 115°C. The carrier gas (N₂) flow was 17 ml/min. A flame ionization detector was used and the peak areas of the pyrolysis products were measured with electronic integrators (Varian 480 or CDS 101). An LKB 2250

TMV Cryo-Microtome was used for cutting insoluble samples. The insoluble samples were weighed on a Sartorius 4431 electronic microbalance.

Samples and Preparation.

The samples used in this work are listed in Table II: a) soluble styrene-butadiene copolymers (SBR) and b) vulcanized SBR samples. The soluble samples (15 mg) were dissolved in 2 ml of toluene. 1 µl (7.5 µg) of the sample was placed on the foil with a 1 µl Hamilton syringe. The solvent was evaporated before pyrolysis.

The vulcanized rubber was cut with the microtome to 5-20 µ-thin samples. These samples were then stamped into circular pieces with a diameter of 1.5 mm and finally weighed on the microbalance; the samples weighed 40-150 µg. Samples were also cut by hand with a safety-blade to 20-50 µ-thin slices, stamped like the previous sample and weighed. These samples weighed 180-360 µg.

The prepared sample was placed in the middle of the platinum foil. The foil was then heated over a heat-lamp, in order to fasten the sample to the foil.

Table II. Characterization of the Different Samples Used

a) Soluble polymers

Sample	Polystyrene w/w%	Polybutadiene w/w%
Cariflex S 1500 ^c	22.5-24.5	75.5-77.5
Calibration sample no. 1 ^d (block copolymer)	25.0	75.0
Calibration sample no. 2 ^d (random copolymer)	25.0	75.0
Calibration sample no. 3 ^d (block copolymer)	48.0	52.0
Calibration sample no. 4 ^d (partial block copolymer)	48.0	52.0
Calibration sample no. 5 (homopolymer)	100.0	—

b) Vulcanized SBR, w/w

Sample ^e	Cariflex	Carbon	Accelerator	Antioxidant	S	Stearic Acid	ZnO
A 1	100.0	50.0	1.5(TMTD)	—	—	1.0	4.0
A 2	100.0	50.0	—	—	1.0	1.0	4.0
A 3	100.0	50.0	1.5(TMTD)	—	1.0	1.0	4.0
A 4	100.0	50.0	—	—	2.0	1.0	4.0
A 5	100.0	50.0	1.5(TMTD)	—	2.0	1.0	4.0
B	100.0	50.0	3.0(CBS)	1.0 (Santoflex 13)	2.0	1.0	4.0
C	100.0	50.0	1.5(TMTD)	1.0 (Flektol M)	2.0	1.0	4.0

^cobtained from Shell Chemicals

^dobtained from Philips Petroleum

^eobtained from Trellborg's Rubber Factory AB

CBS (*N*-cyclohexyl-2-benzothiazolesulfenamide)

TMTD (tetramethylthiuram disulfide)

Flektol M (polymerized 2,2,4-trimethyl-1,2-dihydroquinoline)

Santoflex 13 (*N,N*-(1,3-dimethylbutyl)-*N*-phenyl-*p*-phenyl-diamine)

Results and Discussion

Influence of the Pyrolysis Temperature and Time.

The pyrolyses were made in a temperature interval of 450 to 1200°C. Figure 1 shows the influence of the pyrolysis temperature on the first three peaks and the styrene peak from the pyrogram when pyrolysing vulcanized and unvulcanized SBR. The most abundant peak of the first three peaks was the butadiene peak at temperatures lower than about 900°C. 7.5 µg of the pure copolymer was pyrolyzed. In order to obtain comparable results, the integrator counts obtained at pyrolyses of vulcanized SBR were recalculated to a sample size of 7.5 µg polymer. From these curves the optimum pyrolysis tempera-

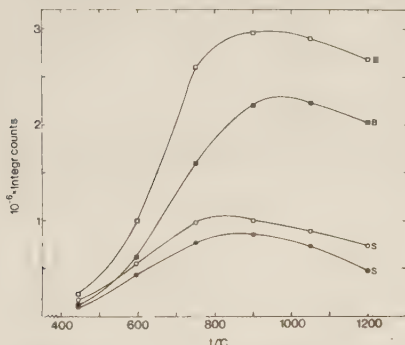


Figure 1. Influence of the pyrolysis temperature on the absolute integrator counts for styrene (S) and the first three peaks (B) from Cariflex S 1500 (see Table IIa) - O, □, - and sample C (see Table IIb) ●, ■. Integrator: Varian 480.

ture could be estimated. In this case the most suitable temperature for the vulcanized SBR was between 900 and 950°C. At this temperature the best reproducibility can be expected. At each pyrolysis temperature the pyrolysis time was chosen to give complete pyrolysis.

The lower yields of butadiene and styrene for the vulcanized SBR depend partly on the larger temperature gradients in these relatively thick samples compared with the pure copolymer, leading to the lower pyrolysis temperatures in these samples. The expected parallel displacement of the curves did not occur probably because of secondary effects at higher pyrolysis temperatures. The total yield differed with about 15%. This indicates that more high boiling products, which do not pass the column, can be formed when pyrolysing vulcanized SBR.

Reproducibility Tests.

The integrator used for these reproducibility tests was a CDS 101. Table III shows the reproducibility of microtome-cut samples. The pyrolyses were carried out over three days on eight samples weighing 57-115 µg, which were pyrolyzed at 900°C for 1 second. The calculations were made using both absolute values ($\bar{x}_A$, S_A) and relative values ($\bar{x}_R$, S_R). The relative value of a peak is the percentage value of its integrator counts relative to the total integrator counts. The integrator counts for the styrene peak showed a smaller variation than for the butadiene peak. The relative standard deviation was 0.8% in absolute values and 0.75% in relative values.

Table IV gives the results from the reproducibility test on hand-cut samples. The pyrolyses were carried out over three days on seven samples weighing 228-316 µg, which were pyrolyzed at 900°C. As the samples were thicker than previous samples, the pyrolysis time had to be 1.2 seconds to give complete pyrolysis. It can be seen that hand-cutting gives a reproducibility that is somewhat poorer than the microtome cutting.

Table III. Reproducibility for Microtome-cut Samples (n = 8) Calculated from the Integrator Counts per µg Polymer. Sample B in Table IIb Weighing 57-115 µg, pyrolyzed at 900°C for 1 sec. Integrator: CDS 101

Peak no.	1+2	3	4	5	6	7	8	9	10
		butadiene							
$\bar{x}_A$	182,066	457,814	123,235	37,357	153,520	19,945	157,963	19,536	69,042
S_A	3.2	2.6	1.3	3.3	1.7	7.7	3.7	7.9	4.9
$\bar{x}_R$	11.10	28.10	7.51	2.28	9.36	1.21	9.85	1.19	4.21
S_R	3.0	2.4	0.96	2.7	1.9	7.1	3.0	7.6	4.4

Peak no.	11	12	13	14	15	16	17	18	Total counts
	styrene								
$\bar{x}_A$	277,213	37,246		25,263	23,527		13,426	9,121	1606,274
S_A	0.80	5.7		4.6	6.4		8.1	16.1	0.78
$\bar{x}_R$	16.91	2.27		1.54	1.43		0.82	0.56	—
S_R	0.75	5.5		4.5	6.5		8.3	16.0	—

$\bar{x}_A$, $\bar{x}_R$ = mean value calculated on the absolute and the relative integrator counts, respectively.

S_A , S_R = standard deviation in percent of the mean value calculated on the absolute and the relative integrator counts, respectively.

Table IV. Reproducibility for Hand-cut Samples ($n = 7$) Calculated from the Integrator Counts per μg Polymer. Sample B in Table IIb Weighing 228-316 μg , pyrolyzed at 900°C for 1.2 sec. Integrator: CDS 101

Peak no.	1 + 2	3 butadiene	4	5	6	7	8	9	10
$\bar{x}_A$	126,881	327,524	99,574	33,584	115,123	21,465	140,339	20,448	65,081
S_A	2.9	2.7	2.2	3.7	3.1	2.4	2.6	9.9	2.7
$\bar{x}_R$	9.72	24.67	7.63	2.57	8.82	1.64	10.75	1.56	4.98
S_R	2.6	2.9	1.9	3.4	2.7	2.4	2.2	10.5	2.4

Peak no.	11 styrene	12	13	14	15	16	17	18	Total counts
$\bar{x}_A$	236,062	13,692	18,385	23,325	17,271	3,760	12,555	7,576	1,282,646
S_A	0.92	3.0	4.0	5.6	11.8	15.5	11.6	14.9	0.88
$\bar{x}_R$	18.09	1.05	1.41	1.78	1.32	0.29	0.96	0.58	
S_R	1.07	3.5	4.2	5.1	11.2	14.3	11.4	15.0	

$\bar{x}_A$, $\bar{x}_R$ = mean value calculated on the absolute and the relative integrator counts, respectively.

S_A , S_R = standard deviation in percent of the mean value calculated on the absolute and the relative integrator counts, respectively.

Influence of the Vulcanization on the Qualitative Analysis.

Figure 2a shows a pyrogram of vulcanized SBR (see sample B in Table IIb) at isothermal conditions on the gas chromatograph. The resolution was improved by temperature programming, resulting in pyrograms like those in Figure 2b (sample B). In Figure 2c a pyrogram from pure copolymer, Cariflex S-1500, is shown. The pyrolysis temperature was 900°C . Peak number 3 is butadiene, peak number 9, vinylcyclohexene (the dimer of butadiene), and peak number 11, styrene. No qualitative differences between vulcanized and unvulcanized SBR could be observed at the GC conditions used.

When a more specific problem is to be solved for a qualitative or quantitative reason, more can be done to improve the resolution on parts of the pyrogram. As the amount of sample at each pyrolysis was different, the peak heights were not directly comparable. The variation in the relative peak heights, however, gave reason for a closer investigation.

Each organic additive in the vulcanized rubber (see Table IIb) was pyrolyzed separately in order to see if they gave any specific peaks for qualitative and quantitative analysis. At high pyrolysis temperatures the main product was $\text{C}_1\text{-C}_3$ hydrocarbons, which all compounded in peak number 1 in Figures 2a and 2b. The contribution was largest for sample B and it was estimated to be at the most 3%.

Most of the differences in distribution (see Table V) must depend on the vulcanization and differences in sample size.

Quantitative Analysis.

Analysis of the composition of the copolymer. The integrator used for this quantitative analysis was Varian 480. Figure 3 shows how the relative value for styrene and the first three peaks vary with the pyrolysis temperature for vulcanized and unvulcanized SBR. The butadiene peak could not be used for quantitative analysis as the vulcanization affects this peak. At the pyrolysis temperature, 900°C , the relative value for the styrene peak was the same for vulcanized and unvulcanized SBR.

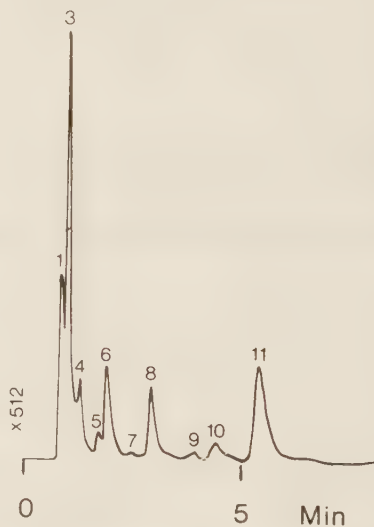


Figure 2a. 80 μg of sample B in Table IIb pyrolyzed at 900°C . Temperature of the column: 150°C isothermal.

Figure 4 gives a calibration curve using unvulcanized copolymers at 900°C . The relative integrator counts of the styrene peak were plotted against the relative weight of styrene in the copolymer. The numbers in the figure refer to the calibration sample numbers in Table IIa. The styrene peak from the vulcanized SBR used in the quantitative analysis had a mean

Table V. Influence of the Sulphur Content on the Relative Values of Nine Pyrolysis Peaks of Interest

Peak no.	S	TMTD	Total	Sample	1	2	3	4	6	8	9	10	11
Sample	w/w	w/w	sulphur content*	amount									
			/%	/μg									
Cariflex S 1500				7.5	6.9	4.0	29.6	5.5	6.8	4.3	0.8	1.8	21.3
A 1	—	1.5	0.51	371	6.4	4.3	18.8	4.4	6.5	7.3	2.1	2.9	15.7
A 2	1.0	—	0.64	391	6.6	4.3	18.8	4.3	6.7	7.3	1.7	3.0	15.8
A 3	1.0	1.5	1.14	354	6.9	4.7	18.2	4.4	6.6	7.6	1.6	3.0	15.2
A 4	2.0	—	1.27	468	6.7	4.4	16.9	4.1	6.2	8.0	1.9	3.4	15.5
A 5	2.0	1.5	1.77	380	7.9	5.0	16.4	4.3	6.7	8.4	1.3	3.2	14.8
		CBS											
		w/w											
B	2.0	3.0	1.24	218.0	8.2	5.2	16.8	4.3	7.6	7.7	1.0	2.8	15.2

* Calculated from the total amount of sulphur available in the sample.

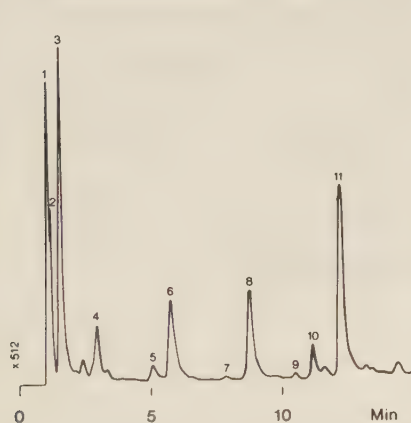


Figure 2b. 218 μg of sample B in Table IIb pyrolyzed at 900°C. Temperature of the column: 50-175°C, 10°C/min.

relative value of 19.0%. In the calibration curve this corresponded to 23.0 weight percent styrene. The polymer producer reports the copolymer to contain between 22.5 and 24.5 weight percent styrene. The values in Figures 3 and 4 could not be compared with the values in Table IV since the different integrators start and stop integration somewhat differently.

Determination of the residue. The amount of the residue from the pyrolyzed vulcanized rubber could be determined. The residue consisted of the non-pyrolyzable substances, carbon black and zinc oxide (see Table IIb). The determination was made by weighing back the residue on the microbalance after complete pyrolysis. It was possible to make residue analysis with a deviation less than 1% from the expected value.

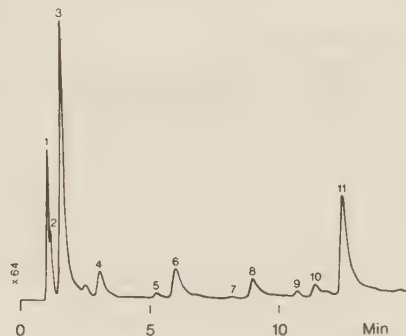


Figure 2c. 7.5 μg of Cariflex S 1500, Table IIa, pyrolyzed at 900°C. Temperature of the column: 50-175°C, 10°C/min.

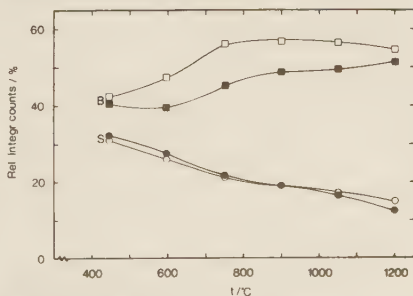


Figure 3. Influence of the pyrolysis temperature on the relative integrator counts for styrene (S) and the first three peaks (B) for vulcanized - ●, ■ - and unvulcanized - ○, □ - SBR. Integrator: Varian 480.

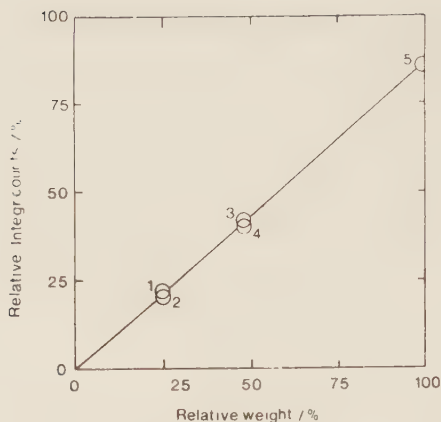


Figure 4. Calibration curve on the styrene peak. Calibration sample numbers 1-5 in Table IIa pyrolyzed at 900°C for 8 msec. Integrator: Varian 480

Influence of the Sulphur Content.

In Table V the results from a test on samples with varying amounts of sulphur and accelerator tetramethylthiuram disulfide (TMTD) are given (see Table IIb). The pyrolyses were carried out at 900°C in 1.2 seconds. As the first peaks were of interest, the resolution was improved by temperature programming (see Figures 2b and 2c). The results in the table are given in relative values.

The effect of varying sulphur content was, as expected, largest for the butadiene peak, since the sulphur, which crosslinks the polymer chains in the vulcanized SBR, is linked to the butadiene. Increasing the amount of sulphur gave decreasing yield. In peak number 1 there was a contribution in the relative value of about 0.2 from TMTD. Sample B contained the accelerator *N*-cyclohexyl-2-benzothiazolesulfenamide B (CBS) and the antioxidant, Santoflex 13, which contributed to the first peak.

The sulphur donating accelerator, TMTD, gives monosulfide bridges and the pure sulphur gives polysulfide bridges during the vulcanization. It would be possible to differentiate these types of crosslinking by identifying the degradation products, a closer quantitative study of the peaks of interest, and kinetic studies. Further investigations are planned.

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A STUDY OF SULFUR BRIDGES IN FILLED NATURAL RUBBER
VULCANIZATES BY PYROLYSIS GAS CHROMATOGRAPHY WITH
FLAME PHOTOMETRIC DETECTION

Eva M. Andersson, Inger Ericsson and Lena Trojer
Department of Analytical Chemistry, University of Lund,
P.O.Box 740, S-220 07 Lund, Sweden

SUMMARY

Natural rubber vulcanizates of two formulations, with sulfur/N-cyclohexyl-2-benzothiazolesulfenamide (CBS) and tetramethylthiuram disulfide (TMTD) respectively, were analyzed by pyrolysis gas chromatography. A sulfur selective flame photometric detector was utilized. The main pyrolysis products were identified as CS_2 and some thiophenes. The yields of the pyrolysis products from the two types of rubber were very different. The yields also varied with the curing time of the rubbers.

INTRODUCTION

The thermal and mechanical properties of vulcanized rubber are strongly affected by the different types of crosslinks [1,2,3,4]. Direct methods for estimation of the structural properties of vulcanizates include measurements of physical properties [5] as swelling [6], creep [7] and stress-strain [8,9]. Specific degradation with chemical reagents, so called chemical probes, are used in combination with stress-strain measurements [5,10,11] for the relative determination of the different types of crosslinks. Despite the existing methods, there is still a demand for improved procedures to determine the types and distribution of sulfidic bridges especially in filled vulcanizates [5,10].

The pyrolysis technique is an established method for polymer analysis [12]. A survey of the technique applied to analysis of insoluble samples, mainly vulcanized rubber has been made [13]. It has been shown that pyrolysis gas chromatography, PyGC, can be used with good reproducibility for the analysis of large [13,14] samples.

It was shown [13] that the sulfur content affected the yield of butadiene when vulcanized styrene-butadiene rubber was pyrolyzed. Häusler and Hube [15] found a correlation between the degree of swelling and the peak ratio toluene/4-vinylcyclohexene from PyGC measurements of vulcanized polybutadiene.

Recently Czybulka et al [16] studied vulcanizates by pyrolysis field ionization mass spectrometry with special attention to the components present in low concentration, viz. comonomers, accelerators, metal oxides and antioxidants.

In the PyGC studies mentioned [13,15] the flame ionization detector was used. The sulfur containing pyrolysis products should be of special interest for the study of sulfur bridges. Sulfur-containing products can be selectively detected with a flame photometric detector [17]. A flame photometric detector has earlier been used together with PyGC for quantitative determination of aliphatic sulfur-containing additives [18]. The additives were extracted from the polymer prior to pyrolysis.

As a first step in the elucidation of the sulfur bridges in filled vulcanized rubbers by PyGC, the sulfur-containing pyrolysis products were studied in the present work.

EXPERIMENTAL

Apparatus and operating conditions

The pyrolyzer consists of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide. The edges of the foil were bent upward at the middle, in order to prevent the sample from falling off the foil. The foil was heated by two current pulses.

The first, 8 ms long, increased the temperature of the pyrolyzer to the desired pyrolysis temperatures. The second, the length of which could be varied, compensated for heat losses so that the temperature of the pyrolyzer was constant. The pyrolyzer was connected directly to the column of the gas chromatograph. After each pyrolysis the glass walls of the pyrolysis chamber was cleaned with acetone.

Pyrolyzer: Foil pulse [19]

Pyrolysis chamber temperature: 70, 115, 175°C

Pyrolysis temperature: 600, 800, 1000 and 1200°C

Pyrolysis time: 0.2 and 0.5 s

Gas Chromatograph: Varian 1860

Column: 3.5 m x 1/8 in., 1.9 mm I.D., stainless steel

Column packing: 10% Carbowax 20 M on Chromosorb W, AW, 80/100 mesh

Column temperature: Programmed 50-250°C, 20°C/min

Flow rates: N₂-20.0 ml/min, H₂-80 ml/min, Air-80 ml/min

Detector: Flame photometric - Micro Tek Instrument Corporation,
Austin, Texas

Detector temperature: 125°C

Integrator: CDS 101

Mass spectrometer: Finnigan 4021

The integrals of the registered peaks, measured by the integrator, are given in integrator counts, i.e.

Samples and preparations

The formulations of the samples investigated are listed in Table 1. The samples named A_R and B_R were used as references as they had been analyzed for the crosslinks by RAPRA [20], Table 2. These samples had been vulcanized for 33, 50 and 66 min at 140°C . The A_R and B_R vulcanizates were treated with propane-2-thiol and piperidine in n-heptane to cleave the polysulfidic crosslinks, and n-hexane-thiol in piperidine to break the poly- and disulfidic crosslinks.

The samples named A and B had been vulcanized at 140°C for 10, 30, 50 and 70 min. They were used to study the influence of the curing time over a longer period. Furthermore, as the formulations were the same as for the A_R and B_R systems, they were used to check the reproducibility of the vulcanization.

The samples were Soxhlet extracted for 24 h with an azeotropic mixture of acetone, chloroform and methanol (3.5:2.9:2.7 by volume) to remove any residues of sulfurous compounds not combined in the polymer network. The samples were cut in small, thin pieces and weighed on a Sartorius microbalance. The samples weighed 30-50 μg .

The total sulfur content of the samples was determined by elemental analysis [21].

The reference compounds for the identification of pyrolysis products were either commercial products or synthetic preparations. Gaseous reference materials were hydrogensulfide and carbonylsulfide (The Matheson Co., Atlanta, U S A) and sulfur dioxide (Alfax AB, Malmö, Sweden). Other compounds were carbondisulfide (p.a., E. Merck AG, Darmstadt, W. Germany), thiophene (Vondelingenplaat, Rotterdam, Holland), methane-, ethane- and n-pentane thiols (Eastman Organic Chemicals, Rochester, New York, U S A), n-propane-, n-butane-, n-hexane thiols and 2-propene-1-thiol (Fluka AG, Buchs, Switzerland), n-monosulfides; $(C_nH_{2n+1})_2S$, $n=1-6$, n-disulfides; $(C_nH_{2n+1}S)_2$, $n=1-5$, 2-methylthiophene and 3-methylthiophene. The compounds were dissolved in acetone ($1:10^3$ by volume). The injection volume was 1 μ l. Some of the solutions were also used to determine the detector response factors.

RESULTS

Test of chromatographic and detection conditions

Column packings of different polarity were tested. Carbowax 20 M on an unsilanized support was found to give a good separation and symmetric peaks of the sulfurous compounds. The sensitivity of the detector increased with decreasing flow rates of hydrogen and air. At too low air flow rates (≤ 60 ml/min) the flame became unstable. Equal flow rates of hydrogen and air of 80 ml/min were found to give a stable signal and high response factors for sulfurous compounds.

The relation between the detector response and the concentration of sulfurous compounds was determined. Eckhardt et al [17] showed that the order of the response of the FPD was much dependent of the gas flows. Therefore different concentrations of carbondisulfide solutions were injected. The logarithm of the registered peak area was plotted versus the logarithm of the amount of carbondisulfide injected. A straight line with the slope 2.0 was obtained. Consequently, the square root of the peak areas should be a linear function of the amount of sulfurous substances. The sulfur to carbon selectivity was estimated to be $4 \cdot 10^5$ from the detector response for carbondisulfide and acetone.

Table 3 shows the molar response factors for some products.

Identification of pyrolysis products

Fig. 1 shows examples of pyrograms obtained from the two vulcanizing systems. No peaks could be specifically ascribed to any of the two vulcanizing systems. The identification was made from comparison with retention data for injected sulfurous compound solutions. Mass spectrometry did not provide reliable identification due to the large background signals from the hydrocarbons. Injection of hydrogensulfide and the thiols on the Carbowax column yielded very irreproducible results, probably due to adsorption or reactions in the chromatographic system [22]. Therefore it was not possible to establish whether hydrogen-sulfide, methanethiol and 2-propene-1-thiol were pyrolysis products from vulcanized natural rubber, which has been suggested earlier [6].

None of the thiophenes, thiols, sulfides and disulfides tested gave retention data corresponding to peak No. 6.

Natural rubber pyrolyzed together with elemental sulfur or TMTD gave much the same pyrolysis products as the A_R -samples. Natural rubber and carbon black together gave negligible peaks.

Pyrolysis chamber temperature

Samples of the A_R - and B_R -vulcanizates were pyrolyzed at chamber temperatures of 70, 115 and 175°C. The pyrograms obtained at 70 and 115°C were very similar. The yields of high-boiling products did not increase at 175°C. Condensation of possible high-boiling sulfurous products was therefore negligible. At 175°C, which is much higher than the vulcanization temperature, 140°C, degradation was observed. A chamber temperature of 115°C was therefore chosen.

Pyrolysis temperature

The samples A_R50 and B_R50 were pyrolyzed at different pyrolysis temperatures. The time was chosen long enough to yield complete pyrolysis for the sulfurous compounds, viz. 0.5 s at 600°C and 0.2 s at the higher temperatures. The yields of the main products are plotted versus the pyrolysis temperature in fig. 2. The total sulfur content of the pyrolysis products are given in Table 4. The response factors given in Table 3 were utilized for the calculations. For the products not given in Table 3 a value of $7.5 \cdot 10^{11}$ (integrator counts)^{1/2} per mole S was used.

Precision

The standard deviations for the different product yields are shown in Table 5. The variation of the yields from samples extracted on different occasions was not significantly greater than those from samples from the same extraction. No significant change of the yields was observed when the foil was changed.

Pyrolysis of different vulcanizing systems

Fig. 3 shows that the peak pattern is completely different for samples of the A and B series. A_R and B_R are the same rubbers as A and B as they were made with the same formulations but on different occasions. The analysis presented in Table 2, shows that the polysulfide content of the A_R is dominating, whereas the B_R series is dominated by the monosulfides according to the method used. A more detailed information of the yields of pyrolysis products is provided in Table 6. Besides the production of products from the original samples (extracted), the effect of the chemical treatment of the A_R and B_R -rubbers is given.

From the yields of the sulfurous pyrolysis products the sulfur content of the samples was estimated, Table 7.

Sulfur analyses

The results from the elemental total sulfur analyses are given in Table 8. The table also shows the amount of sulfur calculated from the formulations, S_{calc} . The components were supposed to be pure. For most of the samples only single determinations were made as the precision of the method should be better than 2%.

DISCUSSION

Sulfur is bound into vulcanized rubber as different types of sulfidic bridges, causing crosslinks of the rubber, but also as cyclic sulfides or as pendent groups which do not take part in the crosslinking [10]. The two vulcanizing systems were chosen to represent materials with different composition of sulfur bridges.

From the Figs. 1, 2 and 3 it is evident that the pyrolysis pattern is quite different for the two curing systems. As all the samples were Soxhlet extracted before pyrolysis, the interferences from the unreacted curing agents could be excluded and the sulfurous pyrolysis products detected should only originate from sulfur combined with the polymer. The fact that reactions between fragments formed during pyrolysis of the mixtures occurred, implies that the sulfurous pyrolysis products formed from combined sulfur could as well be secondary reaction products as pure degradation fragments.

As no specific peaks were found for any of the samples, the pyrolysis conditions were chosen to yield results as characteristic as possible for each sample. Thus, at 1000°C the pyrograms of the samples with varying curing time showed the greatest variations.

Lower energies are needed to break the sulfidic links than to break the carbon links of the polymer chain [2]. At low pyrolysis temperatures ($< 400^{\circ}\text{C}$), where little degradation of the polymer chain is expected, very low yields of detectable sulfurous compounds were obtained. In contrast to the hydrocarbon production [23], repeated pyrolysis at higher temperatures did not increase the yield. This indicates that nonvolatile products, including elemental sulfur, condensed on the walls of the pyrolysis chamber or at the initial part of the chromatographic column. The higher the temperature the greater was the total yields from the A system while for the B system the total yields were relatively constant (Table 4). At 1200°C all the sulfur in the A samples could be accounted for as volatile products, Table 4,8.

The production of carbondisulfide seems to include several reactions. One contribution to the sudden increase of the yield at 800°C for the A system could be sulfur from the polysulfide links starting to react with carbonaceous fragments. For the B system carbondisulfide was formed in high amounts even at low temperatures. Moreover there was no increase at the highest temperatures. This indicates that for the B system another reaction is involved in the carbondisulfide production. Possibly pendent sulfurous groups [10] from reacted TMTD contribute to the production of carbondisulfide. The A system, see Fig. 2, gave only very little carbondisulfide at 600°C in comparison with the B system. The production of carbondisulfide at 600°C could reflect the amount of disulfide bridges of the samples.

The production of thiophenes and peak No. 6 varied with the temperature in essentially the same way for the two systems but with different yields. The A_R system produced about four times more thiophenes than the B_R system. Cyclic monosulfides which are assumed to be present in vulcanized rubber [2,10], could be the origin of the production of the thiophenes. Sulfur atoms from the polysulfide chains reacted with hydrocarbon fragments could also be the source for thiophene formation.

The production of carbonylsulfide varied in much the same way for the two systems with the pyrolysis temperature. Most probably it originates from reactions with the oxygen-containing zinc oxide and/or stearic acid.

After the cleavage of the polysulfide bridges the amount of CS_2 increased about 30% for the A_R system. The reason might be that the propane-2-thiol combines with the sulfur left on the polymer chain to form disulfide bridges [11]. The total amount of sulfur did not change, Table 8. If the average length of the polysulfide bridges is S_4 and two atoms from the thiol are added to the chains while the two central atoms of the bridge leave, the sulfur content should be constant. The amount of thiophenes decreased correspondingly which indicates that sulfur from the polysulfide bridges no longer was available for thiophene formation.

The propane-2-thiol treatment affects the B system in a different way compared with the A system. Both the total yield of pyrolysis products and the sulfur content of the B samples decreased. The explanation could be that there are sulfurous groups from the TMTD, not to be found in the A_R system, which are influenced by the propane-2-thiol treatment. It seems improbable that the B samples would contain any appreciable amount of polysulfide links with more than four sulfur atoms.

After breakage of the disulfide bridges of the B samples the yield of carbondisulfide decreased compared with both the untreated and the propane-2-thiol-treated B samples, Table 6. This would further confirm that disulfide links are a source of carbondisulfide. The results for the A samples are not directly comparable as the pyrolyses were made at 1000°C where other types of reactions seem to dominate. The yield of thiophenes increased noticeably for the B system. Therefore it is tempting to assume that cyclic monosulfides are formed from disulfide bridges treated with hexanethiol. The yield of thiophenes from the A samples was less altered, which is in consequence with the proposed mechanism of thiophenes also being formed from polysulfide sulfur atoms.

The vulcanization of S/CBS systems is known to be slower than that of TMTD systems [24]. Though the origin of the products is not known yet, the progress of the vulcanization is reflected in the product yields, Fig. 3 and Table 6. The slopes of the

curves, Fig. 3, show a slower vulcanizing process for the A sample than for the B sample. This is further indicated by the sulfur content of the extracted samples of the A and B series (see Table 7).

Several parameters could influence the precision of the product yields. Adsorption of sulfurous products (predominantly thiols) on the inner wall of the column and on the surface of the support could not be excluded [22,25]. It was found that the sample size had to be kept within a small interval ($40 \pm 10 \mu\text{g}$) for an acceptable precision. This indicates that the thermal degradation reaction and other reactions are sensitive to the temperature gradient in the sample. An insoluble sample cannot be placed on the bent foil as reproducible as a sample solution can be applied to a flat foil. Inhomogeneities of the samples and catalysis from the Pt-foil could also increase the standard deviation.

The reproducibility of the batches is given by Tables 6 and 8. Lower yields of pyrolysis products and lower total sulfur contents were obtained for the extracted A and B samples than for the extracted A_R and B_R samples. The yield of the pyrolysis products was proportional to the sulfur content of the A_R and A samples. Therefore the variation could be simply explained by different sulfur content of the initial unvulcanized mixtures. The differences between the yields of the pyrolysis products from the B_R and B samples were smaller than the differences

of the total sulfur content of these samples. In addition, the progress of the vulcanization differed between the B_R and the B samples. Thus, the efficiency of the curing agents seems to vary.

The absolute values of the number of crosslinks reported by RAPRA were certainly approximate. They were based on estimation of quantities, which could only be measured with the unfilled material. Thus merely the relative values could be reliable. Furthermore, only the sulfidic crosslinks were taken into account. Carbon-carbon crosslinks could as well be present. Therefore it was not meaningful to make a closer quantitative comparison between the results from the RAPRA analysis and from the pyrolysis.

CONCLUSION

This study has shown that PyGC with a sulfurselective detector could provide valuable information about various types of vulcanizing systems, the progress in the vulcanization and batch reproducibility. A much more detailed study, including measurements on well-defined model compounds, is necessary before any definite qualitative and quantitative determinations could be made. The diagnostic power of the method should increase with selection of a lower pyrolysis temperature and a chromatographic system more suitable for hydrogen sulfide and thiols, e.g. Teflon columns.

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TABLE 1

Formulations of rubber materials. Weight parts per 100 parts of NR.

Vulcanization system	A _{R,A}	B _{R,B}
Natural Rubber, NR	100	100
Carbon Black, SRF	50	50
ZnO	5	5
Stearic Acid	1	1
CBS ^{a)}	0.6	-
Sulphur	2.85	-
TMTD ^{b)}	-	4

a) N-cyclohexyl-2-benzothiazolesulfenamide

b) Tetramethylthiuram disulfide

TABLE 2

Network analysis made by RAPRA. $S_{\text{total}}\%$: total sulfur content % (w/w). $S_{\text{sulfide}}\%$: inorganic sulfur % (w/w).

$S_{\text{C}}\%$: sulfur combined in the network. ϵ : The Moore efficiency parameter defined by $S_{\text{C}}/\text{crosslink density}$.

Vulcanization system Time min ⁻¹	A_R			B_R		
	33	50	66	33	50	66
% polysulfide crosslinks	75	76	51	17	9	5
% disulfide crosslinks	25	24	49	29	31	22
% monosulfide crosslinks	-	-	-	54	60	73
$S_{\text{total}}\%$ (w/w) (extracted)	1.96	2.12	2.22	0.82	0.74	0.80
$S_{\text{sulfide}}\%$	0.20	0.24	0.28	0.02	0.02	0.05
$S_{\text{C}}\%$	1.76	1.88	1.94	0.80	0.72	0.75
ϵ	9.4	9.2	11.6	5.7	4.5	5.1

TABLE 3

Flame photometric detector response factors for
sulfurous compounds.

Substance	(Integrator counts) ¹ per mole S
CS ₂	3.2·10 ¹¹
thiophene	6.3·10 ¹¹
2-methyl-thiophene	8.3·10 ¹¹
3-methyl-thiophene	8.5·10 ¹¹

TABLE 4

Sulfur content % (w/w) obtained from pyrolysis.

Temperature/°C	600	800	1000	1200
A _R 50	0.36	0.64	1.14	2.05
B _R 50	0.53	0.62	0.65	0.52

TABLE 5

The precision obtained for the different pyrolysis
products of the vulcanizate A_R33 during 3 weeks, n = 13.
Pyrolysis at 1000°C for 0.2 s.

Peak no	1	2	3	4	5	6
$\bar{x}/\sqrt{i.c.x} \mu g^{-1}$	2.96	25.4	29.0	11.2	21.2	9.20
S/%	10.7	13.0	8.8	4.4	4.3	11.5

TABLE 6

The obtained yields of the products marked in Fig. 1 for the vulcanizates pyrolyzed at 1000°C for 0.2 s. Samples marked "extracted" had just been extracted with the azeotropic solvent mixture, "polysulfide" were treated to break polysulfidic links before extraction, "disulfide" were treated to break both poly- and disulfidic links before extraction

Peak no	Pyrolysis product	Sample prepara- tion	A _R 33 yield	A _R 50 / $\sqrt{i.c.}$	A _R 66 x μg^{-1}	B _R 33	B _R 50	B _R 66		
1	carbonyl- sulfide	extracted	3.0	3.5	4.8	2.8	2.8	2.8		
		polysulfide	2.8	3.4	2.7	2.5	2.5	2.4		
		disulfide	2.0	2.3	2.7	1.7	1.8	2.1		
2	carbon- disulfide	extracted	25	28	31	45	43	43		
		polysulfide	33	37	35	34	35	35		
		disulfide	22	27	33	25	25	26		
3	thiophene	extracted	29	30	28	6.1	8.1	7.6		
		polysulfide	25	26	27	8.8	7.4	8.0		
		disulfide	20	30	32	11	14	13		
4	2-methyl- thiophene	extracted	11	13	13	2.1	2.8	2.5		
		polysulfide	9.8	12	9.7	2.5	2.2	2.4		
		disulfide	6.6	11	12	3.1	3.7	3.6		
5	3-methyl- thiophene	extracted	21	22	22	5.7	8.0	6.9		
		polysulfide	18	21	17	6.8	6.8	6.9		
		disulfide	12	20	21	8.5	9.5	10		
6		extracted	9.1	9.6	9.0	2.4	3.1	2.9		
		polysulfide	8.3	8.6	8.8	3.2	2.8	3.0		
		disulfide	6.2	8.8	9.7	3.3	3.9	3.6		
			A10	A30	A50	A70	B10	B30	B50	B70
1		extracted	1.1	1.8	2.1	2.3	1.7	1.8	2.4	2.4
2		- " -	6.7	24	26	27	40	36	31	31
3		- " -	10	22	26	24	5.3	5.0	6.1	8.8
4		- " -	4.2	7.9	10	10	1.9	1.8	2.4	3.5
5		- " -	8.7	17	21	20	5.2	5.5	6.5	8.2
6		- " -	3.6	7.5	9.1	8.6	2.4	2.2	2.4	3.1

TABLE 7

Sulfur content % (w/w) obtained from pyrolysis (1000°C , 0.2 s) of samples treated as described in Table 6.

Sample preparation	A _R 33	A _R 50	A _R 66	B _R 33	B _R 50	B _R 66
extracted	0.89	1.14	1.16	0.60	0.65	0.67
polysulfide	0.95	1.04	0.92	0.50	0.49	0.53
disulfide	0.61	0.80	1.01	0.47	0.50	0.51

TABLE 8

Sulfur content % (w/w). S_{calc} : calculated from the sulfurous compounds of the formulations. S_{exp} : found by elemental sulfur analysis.

Vulcanization system	A _R 33	A _R 50	A _R 66	B _R 33	B _R 50	B _R 66	SRF	NR+SRF 2:1 w/w
Untreated samples								
S_{calc}	1.88	1.88	1.88	1.33	1.33	1.33	0	0
S_{exp}	1.97	2.20	2.32	1.57	1.71	1.61	0.46	0.34
Extracted samples	1.87	2.08	2.21	0.94	0.88	1.04		
After polysulfide cleavage	1.85	2.00	2.28	0.81	0.79	0.76		
After disulfide cleavage	1.20	1.67	1.85	0.81	0.83	0.85		
	A10	A30	A50	A70	B10	B30	B50	B70
Untreated samples								
S_{calc}	1.88	1.88	1.88	1.88	1.33	1.33	1.33	1.33
S_{exp}	2.00	1.96	2.11	2.07	1.38	1.36	1.39	1.36
Extracted samples	0.85	1.84	1.85	2.00	0.42	0.50	0.49	0.47

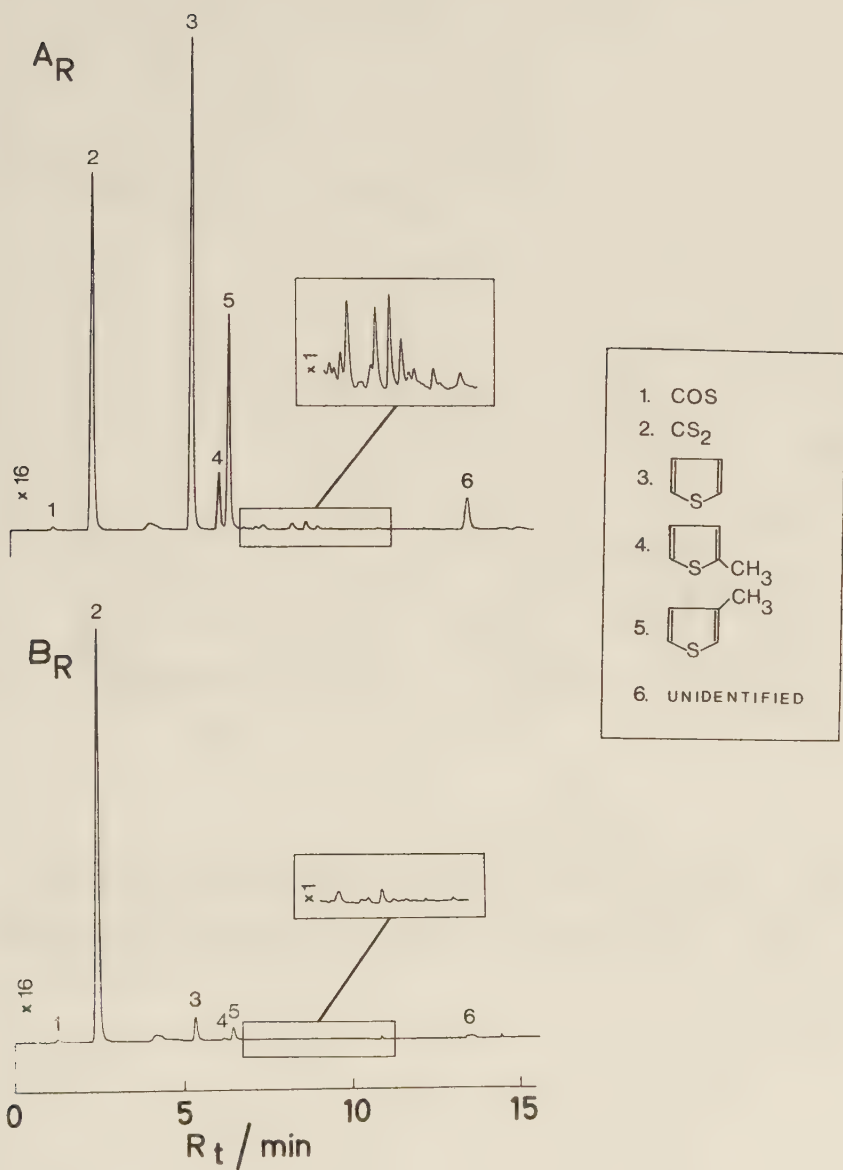


Fig. 1 Pyrograms of 37 μg of A_R^{33} and 33 μg of B_R^{33} pyrolyzed at 1000°C for 0.2 s.

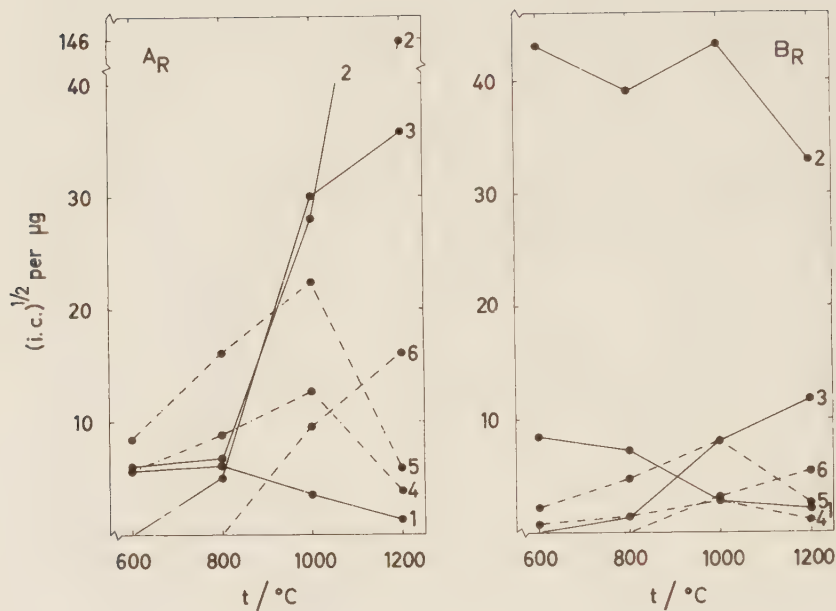


Fig. 2 The yield of the different pyrolysis products marked in Fig. 1 plotted versus the pyrolysis temperature. The samples were A_R50 and B_R50. Pyrolysis time: 0.5 s at 600°C and 0.2 s at the other temperatures.

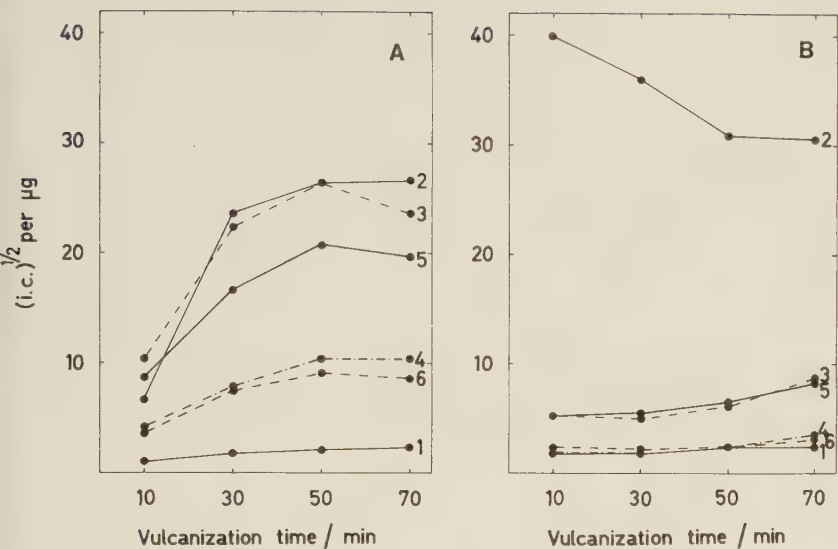


Fig. 3 The yield of the pyrolysis products marked in Fig. 1 plotted versus the vulcanization time. To the left the A series and to the right the B series. Pyrolysis temperature and time: 1000°C and 0.2 s.

CHARACTERIZATION OF REVERSED-PHASE HIGH-PERFORMANCE
LIQUID CHROMATOGRAPHIC STATIONARY PHASES BY MEANS OF
PYROLYSIS-GAS CHROMATOGRAPHY

Lennart Hansson and Lena Trojer

Technical Analytical Chemistry and Analytical Chemistry,
University of Lund, P.O.B. 740, S-220 07 Lund (Sweden)

SUMMARY

Pyrolysis-gas chromatography has been shown to be a valuable tool for the characterization and evaluation of chemically bonded phases for reversed-phase high-performance liquid chromatography. The chain length of the hydrocarbon group bonded to the silica surface could be determined and the functionality of the silanizing agent was established for different C₁₈ materials. The technique could also be used to investigate whether the materials had been post-silanized with reagents such as hexamethyldisilazane for the capping of residual silanol groups.

INTRODUCTION

The development of chemically bonded stationary phases (CBSP) on microporous silica supports for use in high-performance liquid chromatography (HPLC) is one of the major factors that has increased the importance of this technique. Hydrocarbons bonded to the silica support, i.e., phases for reversed-phase chromatography, enjoy great popularity and several reviews on commercial stationary phases have been published^{1,2}.

Because of the increasing number of manufacturers, the type of reversed-phase material for a particular separation is often chosen by chance. However, as frequently pointed out, the packing materials can differ considerably according to their packing characteristics³, their performance^{2,4} and especially their separation properties⁴⁻⁷. Variations from batch to batch for phases from the same manufacturer have also been noted³. Sometimes these differences can be explained in terms of pore size, pore distribution, particle size, particle distribution, surface area, hydrocarbon chain length, hydrocarbon loading, etc., data which are often given by the supplier. However, often the observed differences are not easily explained in these terms⁸.

It has been suggested that the number of unreacted silanol groups on the silica surface can play an important role in reversed-phase chromatography⁹, especially when chromatographing basic substances such as amines^{4,10}.

It appears that more information about the surface properties such as mode of modification (monolayer, polymer layer), functionality of silanizing reagent, chain length of reagent, degree of silanization and degree of "capping" is necessary before a complete understanding of the chromatographic behaviour is possible and a comparison between different reversed-phase stationary phases can be made⁹. Various chromatographic tests

have been employed to evaluate the influence of silanol groups^{8,9} and column performance for comparative purposes¹¹. Screen tests have been used for the evaluation of the separation ability of different bonded phases¹². Methods employed for studying bonded phases, in addition to "standard" elemental analysis, have included IR¹³⁻¹⁶ and photoacoustic spectroscopy¹⁷, UV absorption¹⁸, thermal degradation and mass spectrometry (MS)^{15,19}, alkaline hydrolysis followed by silylation and gas chromatography²⁰ and titration^{21,22}. Unger²³ described various methods for the characterization of HPLC materials.

Pyrolysis-gas chromatography (Py-GC) has found widespread use for the study of polymers²⁴. As the reversed-phase silica support can be regarded as a siloxane polymer modified with hydrocarbons of varying chain length, PyGC should be a useful technique for the study of these materials. A study of silica gels esterified with saturated alcohols by means of Py-GC-MS has been reported²⁵.

In this investigation we used Py-GC for the characterization of reversed-phase silica gels with different chain lengths and structures of the hydrocarbon moiety. We also studied the influence of "capping" on the pyrolysis and chromatographic results.

EXPERIMENTAL

Apparatus

Pyrolyser. The pyrolyser used was a CDS 150 Pyroprobe (Chemical Data System, Oxford, PA, U.S.A.). It consisted of a probe of a platinum-coil type, a quartz tube and a sample holder (see Fig. 1). The sample holder was made by folding a stainless-steel mesh disc for HPLC columns. The probe was inserted into an interface, mounted on the injection port of the gas chromatograph. The interface temperature was set at 275°C. The temperature inside the sample holder was measured by means of an iron-constantan thermocouple.

For identification of the pyrolysis products the pyrolyser was connected to the GC part of a Finnigan 4021 mass spectrometer. The Py-GC-MS measurements were carried out using the same conditions as in the Py-GC investigation except for a change from nitrogen to helium as the carrier gas.

Gas chromatography. A Varian 3700 gas chromatograph with a 1.9 mm I.D. stainless-steel column was used. The carrier gas was nitrogen at a flow-rate of 30 ml/min, and the hydrogen and air flow-rates were 30 and 240 ml/min, respectively. A flame-ionization detector was used at 300°C. The injector temperature was 240°C.

Two GC systems were used: (A) a 1-m Chromosorb 102 column with temperature programming from 50 to 225°C at 20°C/min; and (B) a 2-m column packed with 3% OV-17 on Chromosorb W HP (80-100 mesh) with temperature programming from 70 to 275°C at 20°C/min.

Liquid chromatography. The apparatus, column tubing, fittings and procedure have been described elsewhere²⁶.

Chemicals and packing materials

Octadecyldimethylchlorosilane and octadecylmethyldichlorosilane were purchased from Magnus Scientific (Cheshire, Great Britain). Octadecyltrichlorosilane, vinylmethyldichlorosilane and trimethylchlorosilane were purchased from E. Merck (Darmstadt, G.F.R.). All solvents (E. Merck) were of analytical-reagent grade and all chemicals were used without further purification.

The packing materials studied were LiChrosorb RP-18, RP-8 and RP-2 (E. Merck), μ Bondapak C₁₈ (Waters Assoc., Milford, MA, U.S.A.), Nucleosil C₁₈ (Machery, Nagel & Co, Dürren, G.F.R.), Partisil ODS (Whatman, Clifton, NJ, U.S.A.), Spherisorb ODS (Phase Separations Ltd., Queensferry, Clwyd, Great Britain), ODS-Hypersil (Shandon Southern Products, Runcorn, Great Britain) and Zorbax ODS (DuPont, Wilmington, DE, U.S.A.). The silica gels used to prepare the home-made bonded phases were LiChrosorb Si-100 or Si-60 (E. Merck).

Preparation and capping of CBSP

The bonding procedure used for the preparation of home-made CBSP was basically that used by Hemetsberger et al²⁷ but with variation of the reaction time and the type of original silica gel according to Table I.

The capping of CBSP was carried out in the same way as the preparation of CBSP itself, except that the CBSP was dried at 100°C and 10 mm Hg for 1 h and the reaction time was 5 h.

Pyrolysis procedure

The sample (about 60 µg) was placed in the sample holder of the quartz tube, assembled with the probe and put into the interface. The system was conditioned for about 10 min, during which time any traces of solvents in the sample were evaporated. When a steady baseline had been achieved, the pyrolyser was set at 800°C, whereupon the sample was pyrolysed in 5 sec. Between each run the quartz tube with the sample holder was flushed with a jet of air in order to remove any traces of previous sample.

RESULTS AND DISCUSSION

Gas chromatography

For the purpose of determining the length and type of the hydrocarbon moiety attached to the silica gel, two different GC systems had to be used. Chemically bonded stationary phases with a chain length up to eight carbon atoms were suitably analysed with GC system A. Using this system a good resolution within a reasonable time was obtained. In order to reduce the time of analysis for CBSPs with longer chain lengths, GC system B was employed. This system gave a poor resolution of hydrocarbons below C₈ but was satisfactory for establishing the identity of longer hydrocarbon groups attached to the silica gel.

Pyrolysis conditions

In order to obtain simple pyrograms, i.e., gas chromatograms obtained from pyrolysis products, it would be desirable to be able to choose a pyrolysis temperature at which mainly the C-Si bond was broken while the hydrocarbon chain was left intact (for representative bond energies, see Table II²⁸). As the energy of C-Si bond is dependent on the nature of other groups attached to the silicon atom (see Fig. 2), the splitting pattern will vary with the structure around the silicon atom^{16,28,29}. This is in agreement with our experience. Thus, it appears that an exchange of Si-O bonds for Si-CH₃ weakens the Si-C bond of, e.g., the octadecyl groups, resulting in an increase in the proportion between the C₁₈ and C₁₇ peaks on pyrolysis. Although for some compounds it is possible to choose a low pyrolysis temperature at which the C-Si bond is split in preference to the C-C bonds, it appears that for practical work a higher temperature must be used in order to increase the yield of pyrolysis products. At this temperature both C-C and C-Si bonds are split, as shown by the pyrogram in Fig. 3.

The choice of pyrolysis conditions must be a compromise because of the conflicting demands of a high yield of products and simplicity of the pyrogram. It was found that the optimal pyrolysis conditions for the purpose of this investigation was a set pyrolysis temperature and pyrolysis time of 800°C and 5 sec, respectively. Measurements with a thermocouple (see Apparatus) showed that under these conditions a temperature of about 495°C was reached in the sample holder. Pyrolysis times

longer than 5 sec gave a still increasing temperature. It is thus obvious that the temperature rise time was relatively long and that the pyrolysis of the sample took place during the rise to the set temperature.

Determination of the chain length of the CBSP

Fig. 3 shows the pyrograms of some home-made and commercial CBSPs. Each type of CBSP gave a characteristic pyrogram. The pyrolysis products were a homologous series of predominantly monoalkenes. The formation of alkenes as degradation products from alkanes has been established previously^{16,30,31}. Some workers^{15,19} claim that the Si-O bond is also cleaved at the temperatures used, giving silicon compounds as pyrolysis products. However, such compounds could not be identified as isolated peaks in the pyrograms.

The determination of the chain length of different CBSPs is based on the determination of the chain length of the latest eluted hydrocarbon in the pyrogram, corresponding solely to breaking of the Si-C bond in the CBSP. The determination was accomplished by comparing the retention times with those from a Py-GC-MS run with a C₁₈ CBSP, where the presence and identities of alkenes were confirmed.

Determination of the functionality of the silanizing agent

The fact that the substitution pattern at the silicon atom has a major influence on the bond strength between the silica and the main hydrocarbon chain, as mentioned above, can be utilized to obtain information about the surface structure and the probable functionality (mono-, di- or tri-) of the silanizing agent (see Fig. 2). Fig. 4 shows the pyrograms of three different C_{18} materials synthesized in our laboratory. As can be seen, the peak height ratios of heptadecene and octadecene vary with the type of silanizing agent.

Table III gives the C_{17}/C_{18} peak height ratios of some C_{18} materials. As demonstrated, the ratio falls into three main groups, which is believed to be due to the different functionalities of the silanizing agents. The deviation of the ratios within the three functionality groups (mono-, di- and tri-) could be attributed to different kinds of original silica and, with di- and trifunctional silanizing agents, to different degrees of post-polymerization. The identity of the silanizing agent was confirmed by the manufacturers in some instances. The precision of the peak-height ratio expressed as relative standard deviation was 6% for measurements during 1 day and 10% for measurements during 3 months.

Verification of capping of CBSP

The necessity for subsequent treatment of CBSPs with TMCS or HMDS for the capping of residual silanol groups has been discussed. The results from elemental analysis of the CBSPs do not give a sufficiently large increase in the carbon content to verify that capping takes place³². On the other hand, chromatographic tests indicated that capping does occur and improves efficiency^{33,34}.

Experience from work with CBSPs at this laboratory pointed to a considerable difference in performance between different batches of the same phase, especially when chromatographing basic substances such as amines and amides. This is demonstrated in Fig. 5, which shows the results for a mixture of some urea derivatives run on three different batches of Nucleosil C₁₈ under identical conditions. It can be seen that not only the retentions but also the order of retention are different. It is believed that this behaviour is due to differences in capping of residual silanol groups.

In order to investigate the value of Py-GC for the verification of capping of CBSPs, two kinds of home-made C₁₈ phases, one treated with trimethylchlorosilane (TMCS) and one untreated, were subjected to Py-GC (see Fig. 6). It can be seen that the pyrograms are almost identical, with the exception of the relative height of the methane peak. Thus it is greater for the capped material. The ratio of the peak heights of methane and butene was taken as a measure of the capping efficiency.

Table IV gives the peak-height ratios of the methane/butene peaks for trifunctional capped and uncapped material. Of course, this ratio will vary with the functionality of the silanizing agent. However, as capping is of minor importance for the mono- and difunctional silanizing agents, our investigation has been mainly concerned with the trifunctional one. The precision of this peak height ratio, expressed as relative standard deviation, was 11%.

The three batches of Nucleosil C_{18} mentioned above were pyrolysed (see Fig. 5) and the methane/butene peak-height ratio was determined. The previous investigation (see Table III) indicates that the bonded phase of Nucleosil C_{18} is of the trifunctional type. From Table IV it can be seen that the methane/butene peak height ratio from batches 9101 and 9122 fit well with an uncapped C_{18} phase of the trifunctional type. Batch 8111 seems to be a capped C_{18} phase of the same type and the third batch (0061) seems also to be capped. These observations were later confirmed by the manufacturer.

In Table IV are also tabulated the carbon contents of some of the pyrolysed phases, determined by elemental analysis. It can be seen that the carbon content varies considerably between the different materials investigated. However, this fact does not reveal whether the material is capped or not. In order to try to verify if a packing material is capped on the basis of carbon elemental analysis, a comparison between the carbon contents of a capped and the same uncapped batch must be made.

In Table IV such a comparison was made for the first two packing materials and a slight increase in carbon content was obtained for the capped material. However, it is questionable if this can be taken as a proof of capping, because of the small difference and the fact that it has been stated that the carbon content does not necessarily increase after capping³².

CONCLUSIONS

Py-GC offers a useful method for the characterization of CBSPs on silica gel. The method is rapid and reasonably reliable and can be used without any pretreatment of the samples. The method can be employed for studying both the nature of the hydrocarbonaceous phase and the functionality of the silanizing agent. It is also useful for establishing if the phase has been capped or not and the capping efficiency. It is believed that further quantitative investigations could give a more detailed picture of the structure of CBSPs and such investigations are planned for the near future.

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TABLE I

Materials and conditions used for the preparation of home-made CBSP.

Type of modifier	Designation of product	Type of silica	Particle diameter (μm)	Reaction time (h)
Trimethylchlorosilane	TMCS-silica	Si-100	5	24
Vinylmethyldichlorosilane	VNDCS	Si-60	10	2
Octadecyltrichlorosilane	OTCS-silica	Si-60	5	1.5
Octadecylmethyldichlorosilane	OMDCS-silica	Si-100	5	24
Octadecyldimethylchlorosilane	ODMCS-silica	Si-100	5	24

TABLE II

Bond energies.

Type of bond	Bond energy (kcal/mole)
Si-C	76
Si-O	108
C-C	82.6
C-H	98.7

TABLE III

Determination of probable functionality of different C₁₈ materials by means of Py-GC.

Packing materials	Batch	Mean particle diameter (μm)	Peak-height ratio C ₁₇ /C ₁₈	Probable functionality of silanizing agent
ODMCS-silica*	Home-made	5	0.54	Mono
OMDCS-silica*	Home-made	5	1.24	Di
OTCS-silica*	Home-made	5	3.5	Tri
Zorbax ODS	18341-66	6	0.76	Mono
μ-Bondapack	58	10	1.18	Di
Lichrosorb	VV58	10	1.30	Di
Partisil	100130	10	3.1	Tri
Spherisorb	MH 15/175	10	3.6	Tri
Hypersil	GA 613	5	4.7	Tri
Nucleosil	8111	5	5.1	Tri
Nucleosil	9101	5	7.5	Tri
Nucleosil	9122	5	6.8	Tri

*For explanation, see Table I

TABLE IV

Investigation of capping of some trifunctional C_{18} materials
by means of Py-GC.

Packing materials	Batch	Mean particle diameter (μm)	Peak-height ratio C_1/C_4	Elemental analysis C(%)
OTCS-silica*	Home-made	5	0.40**	17.2
Capped OTCS-silica	Home-made	5	1.60***	18.0
Nucleosil	8111	5	1.22 [§]	14.9
Nucleosil	9101	5	0.49**	13.3
Nucleosil	9122	5	0.42**	13.5
Nucleosil	0061	5	0.99 [§]	13.6
Partisil	100130	10	1.82 ^{§§}	
Spherisorb	MH 15/175	10	0.97 ^{§§}	
Hypersil	GA 613	5	1.36 ^{§§}	

* See Table I

**Not capped

***Treated with TMCS.

[§] Capped according to the manufacturer

^{§§} Probably capped.

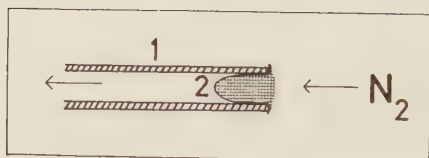


Fig. 1. Diagram showing sample application part placed inside the Pt-coil of the probe. 1 = Quartz tube; 2 = sample holder.

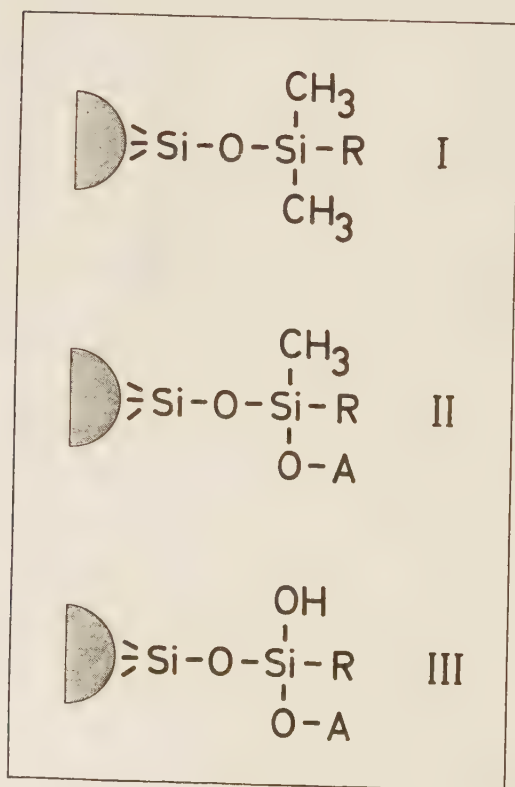


Fig. 2. Schematic formulae of the different structures of CPSPs obtained when mono-(I), di-(II) and tri-(III)functional sila- nizing agents are reacted with the silica surface. R = Hydro- carbon chain; A = H or Si $\rightarrow$.

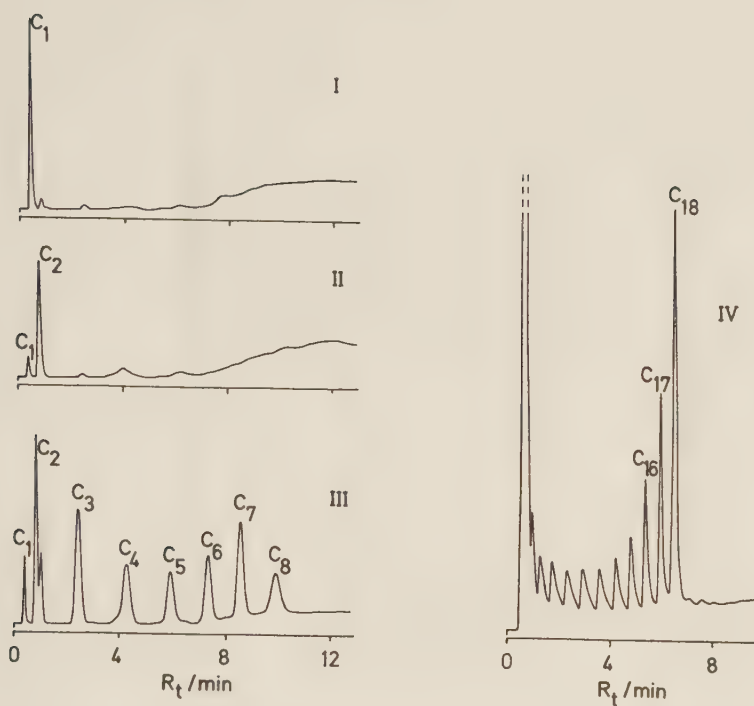


Fig. 3. Pyrograms of CBSPs with different chain length of the hydrocarbon moiety (R). I, R = methyl-, GC system A; II, R = vinyl-, GC system A; R = octyl-, GC system A; IV, R = octadecyl-, GC system B. I, II and IV, home-made CBSP; III, LiChrosorb RP-8.

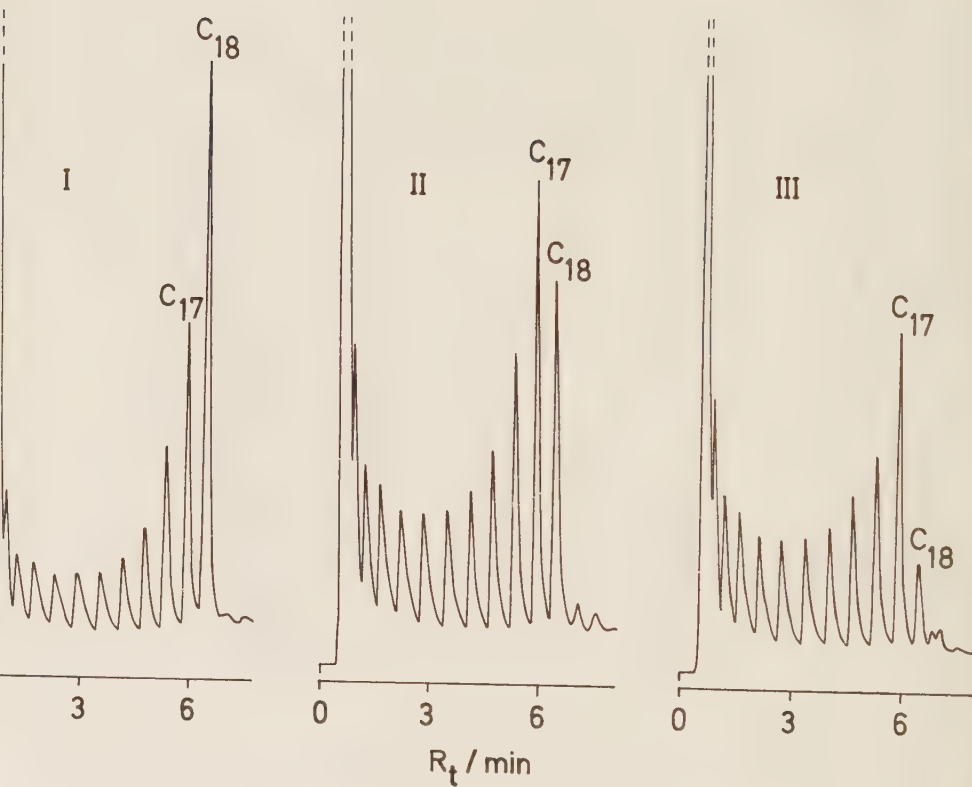


Fig. 4. Pyrograms of three different C₁₈ materials. I = ODMCS-silica; II = OMDCS-silica; III = OTCS-silica. GC system B. For explanation see Table I.

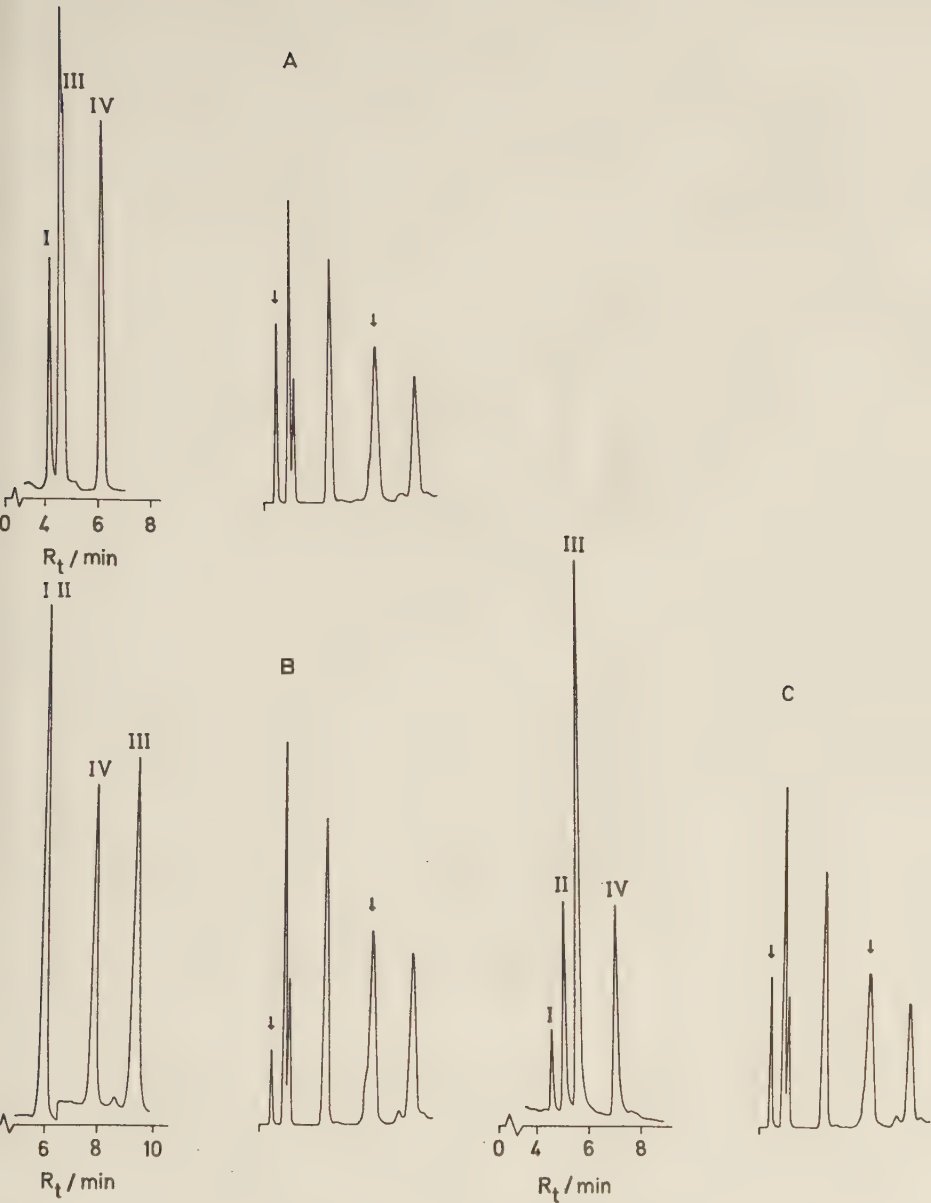


Fig. 5. Liquid chromatogram (left) and corresponding pyrogram (rights) of three different batches of Nucleosil C₁₈ (5 μm). A, Batch 8111; B, batch 9101; C, batch 0061. Batch 8111 and 0061 are capped and batch 9101 is not capped. Liquid chromatograms: urea derivatives of 9-(N-methylaminoethyl)anthracene reagent and (I) toluene 2,6-diisocyanate, (II) toluene 2,4-diisocyanate, (III) hexamethylene diisocyanate and (IV) 4,4'-diphenylmethane diisocyanate; eluent, acetonitrile-water (70:30), the aqueous phase containing 3% of triethylamine, pH 3.0; flow-rate, 2 ml/min; column, 200 x 5 mm Nucleosil C₁₈ (5 μm). Pyrograms: GC system A; the arrows mark the C₁ and C₄ peaks.

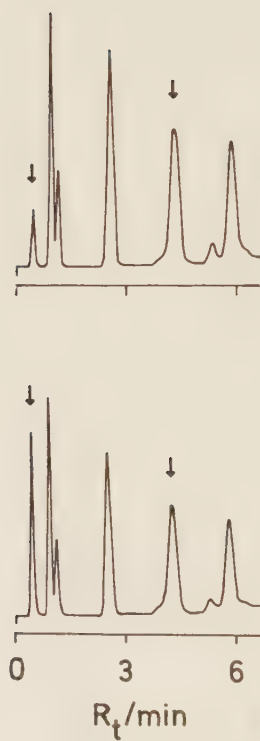


Fig. 6. Pyrograms of OTCS-silica. Top, uncapped material; bottom, capped material. The arrows mark the C_1 and C_4 peaks used for the calculation of the C_1/C_4 peak-height ratios in Table IV. GC system A.

A STUDY OF POLYMERIZATION AND POST SILANIZATION OF
OCTADECYLSILYL PHASES BONDED TO SILICA GEL

Lena Trojer and Lennart Hansson

Analytical Chemistry and Technical Analytical Chemistry,
University of Lund, P.O.B. 740, S-220 07 Lund (Sweden)

SUMMARY

Octadecylsilyl stationary phases bonded to silica gel were studied using pyrolysis-gas chromatography. Polymerization of the phases was confirmed by pyrolysis, although no change in the minimum of a Van Deemter-plot could be verified. Different capping procedures were investigated and the preferred reagent was tetramethylchlorosilane without other reactants. Capping of di- and trifunctional octadecylsilyl phases was established by pyrolysis. The carbon content obtained from elemental analysis confirmed the capping of trifunctional octadecylsilyl phases.

INTRODUCTION

Reversed phase (RP) high performance liquid chromatography (HPLC) constitutes the major technique of the analytical LC separations^{1,2}. In this technique chemically bonded silica is used to a great extent where octadecylsilyl (ODS) bonded silica dominates².

Because of the lack of methods for a chemical characterization, RPLC has been and still is a relatively undefined system in LC³. In a previous paper⁴ we used pyrolysis gas chromatography (PyGC) as a tool for the investigation of the structure of chemically bonded stationary phases (CBSP). Two aspects in that work gave impulses to a further study, namely post silanization or capping and polymerization of especially trifunctional ODS phases.

The ODS bonded silica can be derived either from mono-, di-, or trifunctional octadecylchlorosilanes, octadecylalkoxysilanes or from cyclic polymers. Polymerization (oligomerization), which can occur only for di- and trifunctional CBSPs, has been assumed to occur^{3,5,6}. If the reaction with silica is carried out under anhydrous conditions polymerization is largely prevented. For a well defined CBSP, monofunctional silanizing agents are recommended^{2,7,8}, although such reagents might possess a lower reactivity. One of the aims with the present work is to verify polymerization by PyGC and to test the more or less polymerized ODS phases by LC.

For di- and trifunctional ODS phases one or two unreacted groups per molecule silanizing agent may be left and lead to the formation of additional silanol groups after further hydrolysis. Silanol groups can give rise to mixed retention mechanisms and result in unfavourable effects on e.g. column stability, retention reproducibility and peak asymmetry^{2,9}. By capping with e.g. trimethylchlorosilane the undesirable effects of silanol groups will be reduced^{2,9}. An example of the effect of capping is given in⁴, where PyGC was used to decide whether an ODS phase was capped or not.

EXPERIMENTAL

Pyrolysis conditions

The pyrolyser was a CDS 150 Pyroprobe (Chemical Data System, Oxford, PA, U.S.A.) with a probe of the platinum-coil type. A quartz tube with a sample holder was inserted into the coil. A detailed description is given elsewhere⁴.

For the polymerization study the pyrolysis temperature and -time were set to 800°C and 5 seconds. Measurements with a thermocouple, showed a temperature of 480°C inside the sample holder after 5 seconds.

Optimal pyrolysis conditions for the post silanization study were found to be a dial setting of 700°C, 5 seconds. Measurements of the temperature with the thermocouple showed that this corresponded to 410°C inside the tube after 5 seconds.

Chromatography

The gas chromatographic conditions were the same as before⁴. The liquid chromatography apparatus, column tubing, column packing, fittings and procedure have been described elsewhere¹⁰.

Chemicals

Octadecyldimethylchlorosilane (ODMC) and octadecylmethyldichlorosilane (OMDCS) were purchased from Magnus Scientific (Sandbach, Cheshire, Great Britain). Octadecyltrichlorosilane (OTCS), trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDS) were purchased from E. Merck (Darmstadt, W. Germany) and trimethylsilylimidiazole (TMSI) from Fluka (Buchs, Switzerland). The silica gel used to prepare the bonded phases was Lichrosorb Si-100, 5 μ m (E. Merck) from the same batch (F 1643) and charge (9651043).

Preparation, polymerization and capping of CBSP

The bonding procedure used to prepare the different CBSP was basically that used by Hemetsberger et al.¹¹ but with some variation of the reaction conditions. If nothing else is stated the bonding procedure was carried out by adding 90 ml of toluene (Na-dried), 8 mmol of silane and 5 ml of pyridine (KOH-dried) to 4 g of silica (dried over night at 220°C in air). The mixture was refluxed for 6 hrs under dry nitrogen. The mixture was stirred with a glass rod during the reaction. A funnel with a sinter glass bottom was used for the washing of CBSP with successive batches of toluene, chloroform, methanol, methanol/H₂O, acetone and diethylether.

For the polymerization study one batch (I) was made under extra dry conditions to prevent the formation of polymers. Approximately 5 ml of toluene was distilled off from the reaction vessel to remove any trace amounts of water on the walls before the reaction was carried out. This batch is referred to as "monomeric". Another batch (II) was prepared under normal dry conditions¹¹. To obtain bonding with polymerization for the third batch (III), 150 μ l of H₂O was added to the reaction vessel after 2 h and another 150 μ l of H₂O after 4 h. This batch is referred to as "polymeric". To prepare CBSP from octadecyldimethylchlorosilane, the reaction time was extended to 24 h.

The capping of the CBSP was carried out in the same way as the preparation of CBSP itself except that 0.5 g of CBSP was dried at 100°C in air over night and 1 ml of trimethylchlorosilane, 20 ml of toluene and 1 ml of pyridine were added to the reaction vessel.

In two other capping procedures 0.5 ml of trimethylchlorosilane and 1 ml of hexamethyldisilazane or 0.5 ml of trimethyl chlorosilane and 1 ml of trimethylsilylimidiazole were used as silanizing agents. A blank was prepared using the same procedure, except that the silanizing agent was omitted. All samples were dried at 120°C, 3 mm Hg for 30 min prior to pyrolysis or elemental analysis.

RESULTS AND DISCUSSION

Polymerization of the ODS phase

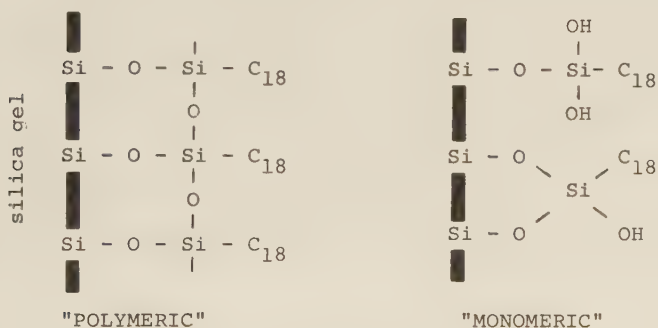
In our previous work the peak height ratios between heptadecene (C_{17}) and octadecene (C_{18}) in the pyrogram were found to fall into three main groups due to mono-, di- or trifunctionality of the ODS phase⁴. It is well known that the Si-C bond strength varies with the substitution pattern at the Si atom¹². A Si-O bond, compared to a Si-CH₃ bond, will strengthen the Si-C bond of the octadecyl group resulting in an increased C_{17}/C_{18} peak height ratio. Within the group of trifunctional ODS phases the variation in the C_{17}/C_{18} peak height ratios was believed to be due to different kinds of original silica materials and to different degrees of polymerization of the phase.

Fig. 1 shows the pyrograms of the three batches (I, II, III) of ODS phase made under the different conditions described in the experimental part. The fragmentation pattern was dominated by a homologueous series of mainly monoalkenes⁴.

The peak height ratios C_{17}/C_{18} for the three ODS phases are given in Table I. The variation in the ratios was about 6%, expressed as relative standard deviation. The peak height ratios for the trifunctional reagent are significantly different for the "monomeric" and the more or less "polymeric" ODS phases.

The result from the elemental analysis of the carbon content is also given in Table I. It can be seen, that despite the addition of water and an excess of silanizing agent, the carbon

content is almost the same as that of the "monomeric" phase. The coverage seems to depend more on the number of surface silanols than on the reaction conditions. The fact that tri-functional ODS phases, prepared under different conditions, give distinctly different C_{17}/C_{18} peak height ratios while the carbon content is almost unchanged, might be explained by the following structure patterns.

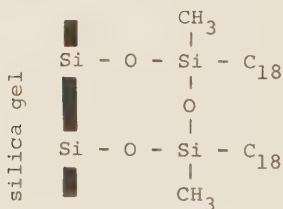


It has been shown earlier that even if the starting material for the silanization was a polymer, the chain could be broken by acids or bases and give the same carbon content as if the starting material was a monomer¹³.

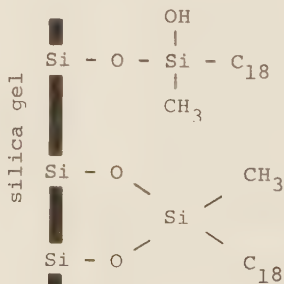
Fig. 2 shows the separation of a test mixture on identical columns except for the packing materials, which were the tri-functional ODS phases, batches I, II, III. Retention times, plate numbers and assymetry factors are given in Table II. It is evident that the efficiency of the column and resolution of the test mixture for the "polymeric" phase was not poorer than for the "monomeric" phase. A slight increase of the retention times could be observed for the "polymeric" phase, however.

It has been proposed that a so called chromatographically evidenced polymeric phase would give a slow mass transport between the mobile and the stationary phase. This would change the minimum in the Van Deemter plot to lower flow rates and in addition the slope on the ascending part of the plot would be steeper³. Plots of HETP versus flow rate for two identical columns packed with "monomeric" and "polymeric" ODS phase, respectively, were made. It appeared that the HETP-minima were the same for the two phases. There were some differences in slope of the ascending part of the curve but the plot was steepest for the "monomeric" phase, i.e. opposite to what would be expected if the conception "chromatographically evidenced polymeric phase" had the same meaning as "polymeric" in this work.

In the case of difunctional silanizing agents a polymeric reaction is limited to formation of a dimeric siloxane as illustrated below



"OLIGOMERIC"

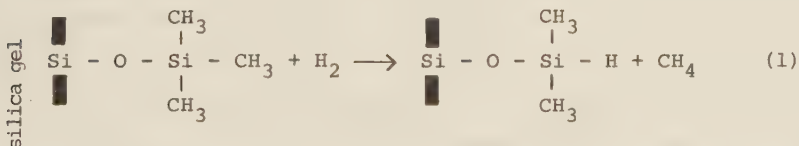


"MONOMERIC"

This is also supported by the results from the "polymeric" difunctional ODS phases. Almost the same C_{17}/C_{18} peak height ratios were obtained (see Table I).

Postsilanization

To obtain maximum information about the capping, a lower pyrolysis temperature was chosen compared to that used in the polymerization studies. It is known^{7,14} that thermal degradation of alkylsilyl bonded silica yields alkylsiloxanes. However, as alkylsiloxane products could not be detected in the used GC system, the production of methane was utilized as an indicator of the efficiency of the capping procedures. A trimethylsilyl group bound to silica is degraded according to the following scheme



Hydrogen is normally present during pyrolysis of hydrocarbons¹⁵ or water. Methane can also be produced from the C_{18} chain of the ODS phase. The extent to which equation (1) occurs was found to depend on a number of factors including whether the trimethylsilyl group is bound directly to silica as in eq (1) or is bound to CBSP. It is therefore not possible to determine the absolute amount of trimethylsilyl groups from the amount of methane produced. However, a relative measure was obtained by taking the ratios of the C_1 to C_3 peak heights.

A study of the efficiency of different capping methods was made on trifunctional ODS phases and the results are shown in Table III. The variation in the peak height ratio was 6% expressed as relative standard deviation. The efficiency of the tested silanizing agents seems to be almost equal with a slight preference for the capping by only trimethylchlorosilane (TMCS). Hexamethyldisilazane (HMDS) or trimethylsilylimidiazole (TMSI) together with TMCS are generally supposed to enhance the capping reaction as HMDS and TMSI produce a base and TMCS an acid. However, such an enhancement was not supported by our results.

The capping efficiency on ODS phases of varying functionalities was also tested, see Table IV. For uncapped mono-, di- and trifunctional ODS silica there is an increase in the C_1/C_3 peak height ratios which can be attributed to the increasing number of methyl groups attached to the silicon atom holding the C_{18} group. The yield of methane for the uncapped trifunctional ODS silica originates from the degradation of the C_{18} hydrocarbon chain. As the bond strength of the Si-C bond depends on the substitution pattern of the silicon atom, the yield of methane from the ODS phases with different functionalities are not expected to be proportional to the number of methyl groups linked to the silicon atom.

The results from the pyrolysis of difunctional ODS silica indicate that capping indeed occurs although, of course, to a smaller extent than for the trifunctional ODS phase. The carbon content gives very little information about the capping of the difunctional ODS phase. The capping of the monofunctional

ODS phase resulted in a small decrease in the peak height ratio. The carbon content (Table IV) also decreased after capping. The conclusion is that the capping procedure results in a loss of hydrocarbon, which might be due to a split in the C_{18} hydrocarbon chain and/or an exchange of an octadecyldimethylsilyl group for a trimethylsilyl group.

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TABLE I

POLYMERIZATION OF DIFFERENT DI- AND TRIFUNCTIONAL ODS PHASES.

Packing material	Batch nr	Peak height ratio, C_{17}/C_{18}	Mode	Elemental analysis C(%)
OTCS-silica	I	5.8	"Monomeric"	16.7
OTCS-silica	II	3.9		16.6
OTCS-silica	III	2.7	"Polymeric"	17.1
OMDCS-silica	IV	1.9	"Monomeric"	
OMDCS-silica	V	2.2	"Polymeric"	

TABLE II

PLATE NUMBERS AND ASYMMETRY FACTORS FOR DIFFERENT TRIFUNCTIONAL ODS PHASES

Peak*	Batch	t_R /min	Plate number, N^{**}	Asymmetry factor, A_S
B	I	5.8	6800	4.2
	II	5.7	6600	2.5
	III	6.3	8000	2.4
C	I	8.0	7500	3.0
	II	8.0	6900	2.0
	III	8.9	9300	2.9

*see Figure 2

**derived from $N = 5.54 \left(\frac{t_R}{w} \right)^2$, w measured at half the peak height.

TABLE III

INVESTIGATION OF THE CAPPING PROCEDURE FOR TRIFUNCTIONAL
ODS PHASES.

Capping procedure	Peak height ratio, C_1/C_3
Blank	0.42
TMCS	1.07
TMCS + HMDS	0.93
TMCS + TMSI	0.90

TABLE IV

INVESTIGATION OF THE CAPPING OF MONO-, DI- AND TRIFUNCTIONAL
ODS PHASES

ODS phases	Peak height ratio, C_1/C_3	Elemental analysis C(%)
Trifunctional	0.38	16.7
Trifunctional capped	1.30	16.9
Difunctional	0.75	17.2
Difunctional capped	1.00	16.3
Monofunctional	2.1	16.8
Monofunctional capped	1.9	14.5

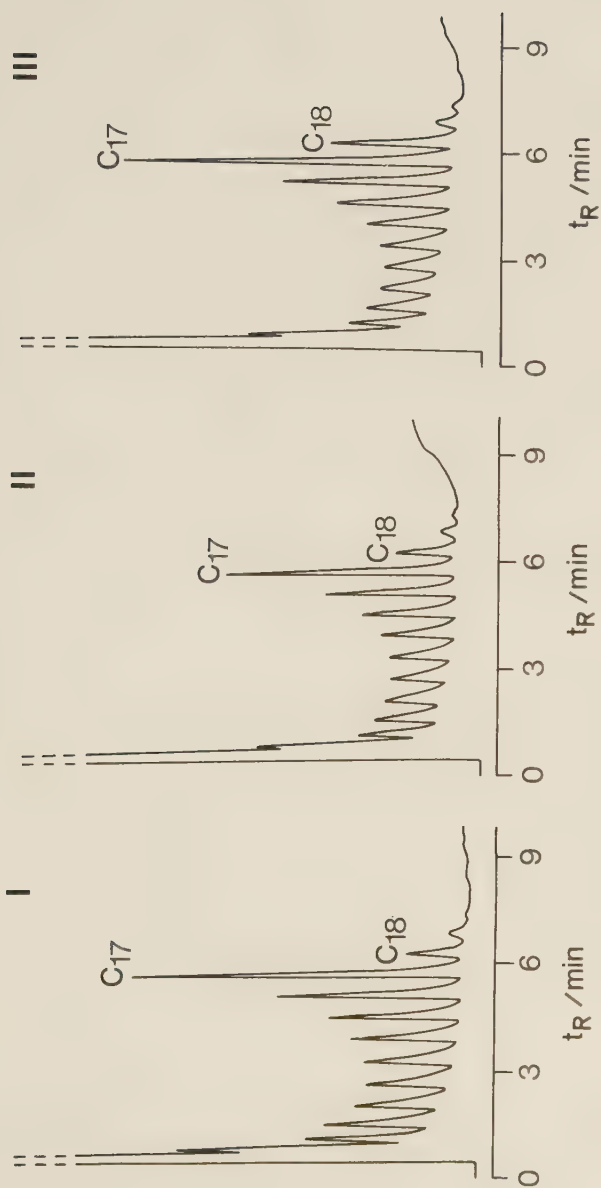


Fig. 1. Pyrograms of three different trifunctional ODS phases I = Batch I (monomeric); II = Batch II; III = Batch III (polymeric). GC conditions: 2 m column with 3% OV-17 on Chromosorb W HP, programming: 70-275°C, 20°C/min.

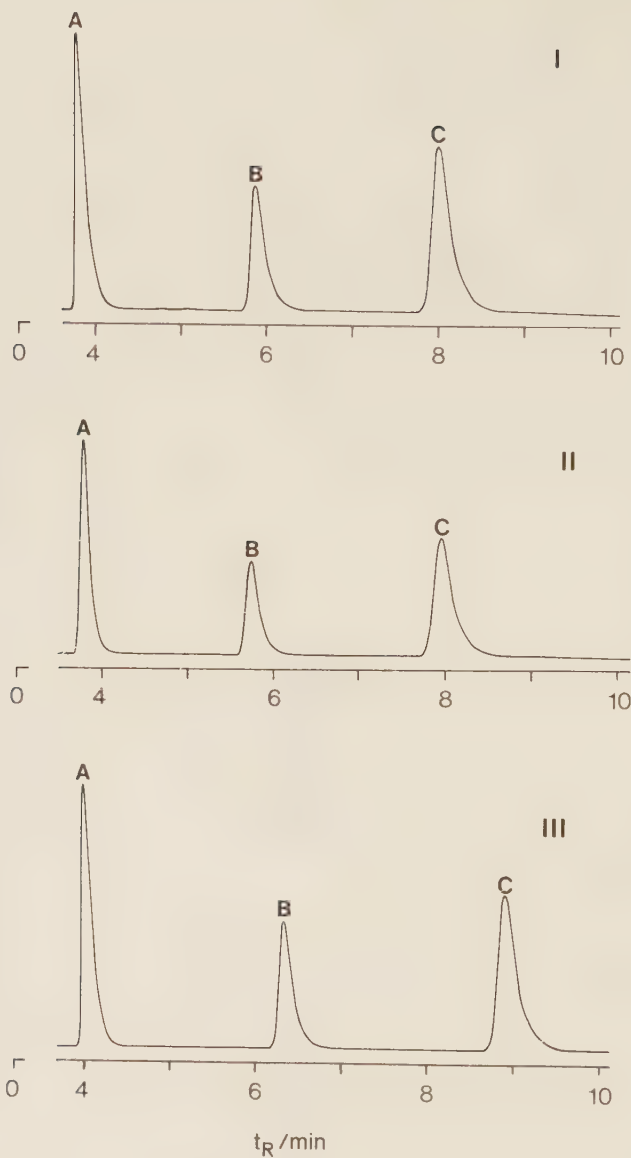


Fig. 2. Liquid chromatogram of three different batches of trifunctional ODS phases. I = Batch I (monomeric); II = Batch II; III = Batch III (polymeric). Samples: A = phenol; B = 2,6-dimethyl-phenol; C = 4-tert. butyl-phenol; eluent, methanole-water (70:30); flow-rate, 1 ml/min; column, 200 x 5 mm.

